INSTRUCTION

IN

CHEMICAL ANALYSIS.

(Qualitative.) $15\text{-}95\text{-}$

BY

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WITH

A PREFACE BY PROFESSOR LIEBIG.

EDITED BY

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MDCCCL.

EDITOR'S PREFACE

THIRD EDITION.

EVERY successive edition of this work must necessarily be in advance of all former editions. The science itself is in a state of continual progress. The author, occupying a distinguished position in the foremost rank of chemists, whose original labours perpetually extend its boundaries, of course includes the latest discoveries in his scientific instructions. He supervises every sheet of my translation, incorporating as we proceed, every fact ascertained, and every improvement devised in the processes. The work, therefore, represents the state of the science at the moment we go to press; and in this respect, as well as in its other transcendent merits, is unrivalled.

If anything were needed in the former editions, it was a simple method of arranging the numerous references in the systematic course; this defect is now supplied. A marginal number is printed to each paragraph, which will greatly facilitate the student in turning from one point to another, and tracing his path through the various processes.

<div align="right">J. LLOYD BULLOCK.</div>

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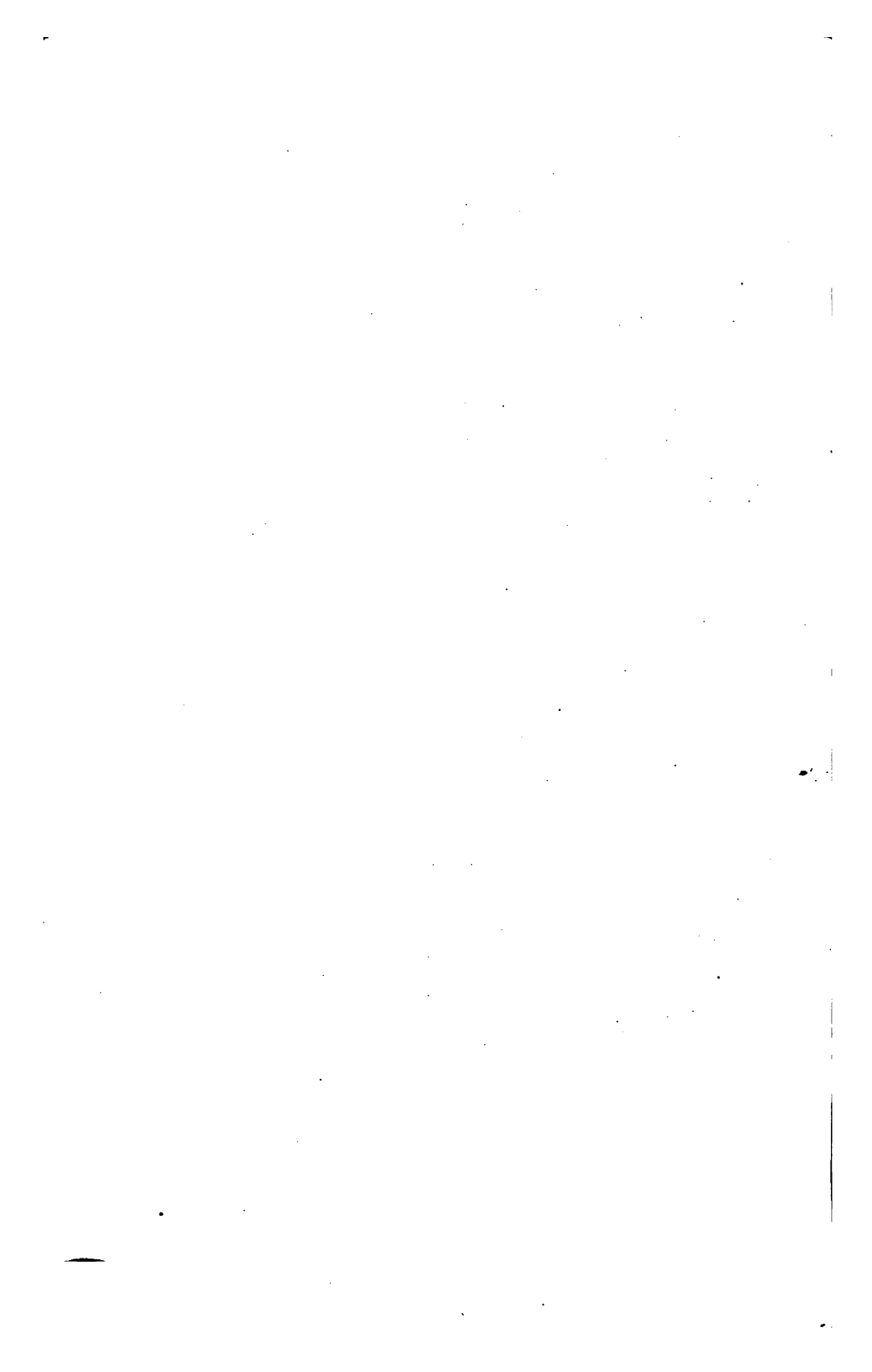
EDITOR'S PREFACE

SECOND EDITION.

THE rapid sale of the first English Edition of this Work has justified the anticipation of the illustrious Chemist, at whose suggestion I undertook to place it at the service of the English student of chemistry. The numerous commendations it received from the press, I may be allowed to say, in my capacity of Editor, it fully deserves. The present edition is almost a new work, so numerous and important are the additions and alterations which are so incorporated into its structure that they could not be produced separately. It represents the FOURTH German edition. Several new works on the same subject, of various pretensions, have made their appearance in this country since this was published—they have not retarded, on the contrary they seem rather to have facilitated its sale.

The increasing taste for practical chemistry, indicated by this efflux of books, calls especially for works detailing methods which may be safely followed and implicitly relied on. I venture to affirm, that in this respect, the work of Dr. Fresenius is pre-eminent. Moreover, those works intended particularly for the use of

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students who enjoy the advantage of tuition in a laboratory, omit
many things which it is absolutely necessary for him to know
from some source.   Indeed this is the only work in the English
language adapted for self-instruction.   With a previous general
acquaintance with chemistry, derived from attendance on a course
of lectures, or from the perusal of some introduction to the science
of which many excellent ones exist, any person may take up this
work, and make himself an expert analyst.   And after all the
assistance given by a teacher, the chemist, when left to his own
resources, still requires a guide to whom he may safely have re-
course for facts which have escaped his memory.   Both as a syste-
matic coure of study, and as a book of reference, Dr. Fresenius's
work is unrivalled.   It has been duly appreciated, since it is
now translated into most European languages, and reprinted in
America.

<div align="right">J. LLOYD BULLOCK.</div>

22, Conduit Street, May, 1846.

PREFACE

BY PROFESSOR LIEBIG.

DR. FRESENIUS conducts the course of elementary instruction, in mineral analysis, in the laboratory of the University of Giessen. During the two last sessions he has followed the method described in his work, entitled, " Elementary Instruction in Qualitative Chemical Analysis." This method I can confidently recommend from my own personal experience to all who are desirous of obtaining instructions in inorganic analysis, for its simplicity, usefulness, and the facility with which it may be apprehended.

I consider Dr. Fresenius' work extremely useful as an introduction to Professor H. Rose's excellent manual, and for adoption in institutions where practical chemistry is taught, but it is especially adapted to the use of Pharmaceutical Chemists.

Further, a number of experiments and discoveries have been recently made in our laboratory, which have enabled Dr. Fresenius to give many new and simplified methods of separating substances, which will render his work equally welcome to those who already are familiar with the larger words on inorganic analysis.

<div align="right">JUSTUS LIEBIG.</div>

EDITOR'S PREFACE.

THIS work of Dr. Fresenius has already gone through two editions in Germany. The abundant opportunities enjoyed by its author of discovering the wants felt by students in entering upon the practice of chemical analysis, and his position in the school at Giessen, has enabled him to devise a method of study of the highest value. That it has received the approbation of the illustrious HEAD of that school, and the benefit of three years practical experience under his immediate observation, must powerfully recommend it to the English student of chemistry. Whoever is desirous of obtaining the knowledge necessary to become a practical chemist, will be in no small degree indebted to Dr. Fresenius for the facilities thus afforded him. Every one who knows anything of Giessen, will bear testimony to the rigid economy of time, and the resolute adoption of every improvement in method which characterise that school, and serve to accomplish the many chemists annually flocking there for the completion of their studies. The author, in his preface to the first edition, tells us that he was led to compose this volume upon perceiving that the larger works on chemical analysis, such as H. Rose's, Duflos', and others, although admirable in themselves, present great difficulties to beginners, which difficulties may be summed

up under three heads; 1st, Too great copiousness and detail; 2nd, The absence of explanations of the causes of phenomena, i. e. the *theory* of the operations and reactions; and 3rd, The omission altogether of many substances of very frequent occurrence, especially in the operations of the pharmaceutist, such as the organic acids, &c.

In avoiding these objections to former works on chemical analysis, Dr. Fresenius, I think, is not chargeable with having fallen into the opposite extreme of being too concise or elementary.

The student may, perhaps, at first be disappointed in taking up this work, to find that there are no tables constructed to fur-nish him at a glance with all he is desirous to know of tests and reactions, and to save him, as he may think, trouble and time. But this has not arisen from oversight; the question of the advantage or disadvantage of tables to the student has been fully considered, and the author has decided,—and the decision is borne out by the highest authorities,—that such tables serve no really good purpose; they rather, on the contrary, supply but very superficial information, and satisfy the student before they have really informed him. The information contained in this work, like every other professing to teach a practical science, requires application and perseverance to attain; but if begun at the beginning, if the student will carefully go over the neces-sary preliminary facts, the examination of his tests, and the reaction of the simple bodies consecutively, and make himself master of this very simple and elementary part of the course, he will find few or no difficulties when entering upon the more elaborate, and—what might appear, without this preparation— complex and intricate processes of the second part, the analysis of compound bodies. It is altogether another question whether

the student should or should not exercise himself and his memory by tabulating the results of his experiments as he proceeds; and to this question we reply in the affirmative; but it must be left to individuals to act in this, according to their own judgment, and their own feeling of its necessity.

In the preface to the Second Edition, Dr. Fresenius tells us that his work has met with much success, having been adopted in the Pharmaceutical Institution of Bonn, &c., as well as in the laboratory of Giessen; and that he has improved it by many corrections and additions.

For my own part, I may be allowed to observe that the English edition was undertaken by the express desire of Professor Liebig, who kindly recommended its being intrusted to my care. The author has supplied me with many corrections, and some additions, and the hope is shared by us in common that it will facilitate the study of analytical chemistry to the English student, and in every way serve to promote the interests of the science.

<div style="text-align: right">J. LLOYD BULLOCK.</div>

22, Conduit Street, October 1, 1843.
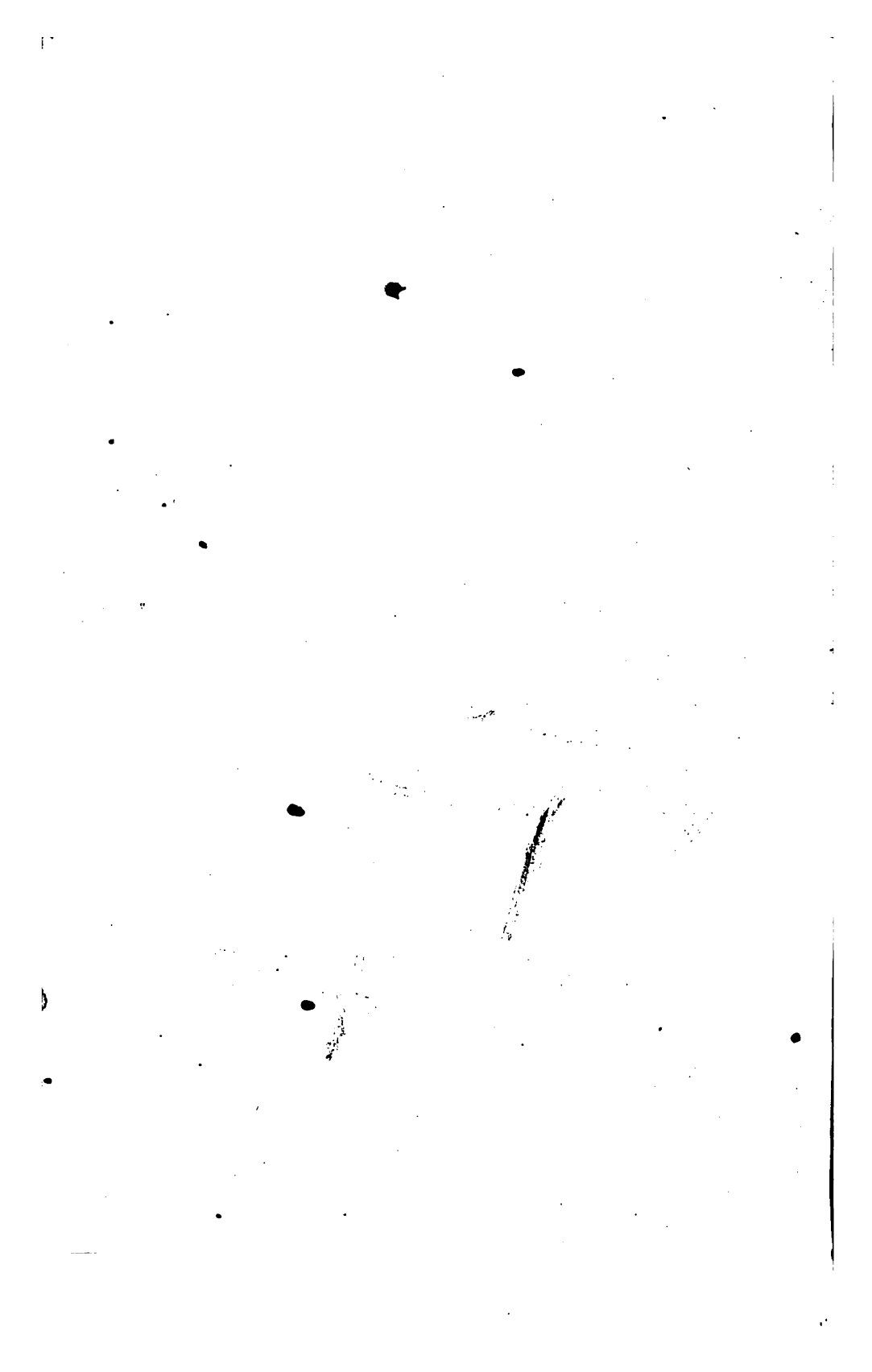
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PART I.

INTRODUCTORY PART.

PART II.

SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.

ELEMENTARY INSTRUCTION

IN

QUALITATIVE CHEMICAL ANALYSIS.

PRELIMINARY REMARKS.

DEFINITION, PURPOSES, OBJECT, AND IMPORTANCE OF QUALITA-
TIVE CHEMICAL ANALYSIS, AND CONDITIONS WHEREON A
SUCCESSFUL STUDY OF THIS SCIENCE DEPENDS.

CHEMISTRY is that science which treats of the various sub-
stances constituting our earth, of their composition and decom-
position, and of their mutual relations and deportment in general.
A special branch of this science is designated by the name of
analytical chemistry, inasmuch as it has a definite object in
view, viz., the analysis of compound bodies, and the investiga-
tion of their constituents. If this investigation is confined to the
nature and *properties* of the latter, the analysis is called *qualita-
tive;* but if the *quantity* of every individual element is to be
ascertained, the analysis is termed *quantitative*. The object of
qualitative analysis, therefore, is to exhibit the constituent parts
of an unknown substance in forms *already known*, and which
consequently admit of safe inferences as to the nature of every
individual element. The value of its method depends on two
circumstances, viz., it must attain the object in view with unerring
certainty, and in the most expeditious manner. Whereas, it is

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the object of quantitative analysis, to exhibit the elements, revealed by the qualitative investigation, in such forms as admit of the most accurate determination of their individual, and proportional, amount or weight.

The ways and means by which these distinct objects are respectively attained, differ much from each other. It is obvious, therefore, that the study of qualitative analysis must be separated from that of quantitative analysis, and, as a matter of course, must precede it.

Having thus generally defined the design and objects of qualitative analysis, I will now proceed to discuss briefly, in the first place, the preliminary information which qualifies students to cultivate this branch of science successfully, the rank which it occupies in chemistry, the objects to which it applies, and the advantages derived from it; and, in the second place, the main points whereon its study is based, and the principal parts into which it is distributed.

It is, above all, absolutely indispensable for the pursuit of qualitative investigations, that the student should possess some knowledge of the chemical *elements*, and of their most important combinations, as well as of the principles of chemistry in general, combined with a certain readiness in the apprehension of chemical processes. The practical part of this science demands, moreover, strict order, great neatness, and a certain skill in manipulation. If the student combines with these qualifications the habit of invariably ascribing the failures with which he may happen to meet, to some error or defect in his operations, or, in other words, to the absence of some condition or other indispensable to the success of the experiment,—and a firm reliance on the immutability of the laws of nature cannot fail to create this habit,—he possesses every requisite to render his study of analytical chemistry successful.

Now, although chemical analysis is thus based on general chemistry, and cannot be cultivated without some previous knowledge of the latter, yet, on the other hand, we must consider it as a kind of *corner stone*, upon which the entire structure of this science rests; for it is almost of equal importance for all

branches of theoretical, as well as of practical chemistry; and I need not expatiate here on the advantages which the physician, the apothecary, the mineralogist, the rational farmer, the manufacturer, the artisan, and many others, derive from analytical chemistry.

This alone would be a sufficient reason to recommend a thorough and diligent study of this branch of science, even if its cultivation lacked those attractions which it unquestionably possesses for every one who devotes himself zealously and ardently to it: The human mind is constantly striving for the attainment of truth; it delights in the solution of enigmas, and where do we meet with a greater variety of problems, more or less difficult of solution, than in the province of chemistry? But as a problem, for which, after long pondering, we fail to discover the key, wearies and discourages the mind,—so, in like manner, do our chemical investigations, if we fail to attain the object in view, if our results do not bear the stamp of truth,—of unquestionable certainty. A *half-knowledge* is therefore, as indeed in every department of science, but more especially *here*, to be considered worse than no knowledge at all; and a mere *superficial* cultivation of chemical analysis is consequently to be particularly guarded against.

A qualitative investigation may be made with a twofold view, viz., either, 1st, to prove that a certain definite body is or is not contained in a substance, e. g. lead in wine; or, 2nd, to ascertain *all* the constituents of a chemical compound or mixture. Any substance whatever may, of course, become the object of a chemical analysis.

In the present work, however, we purpose to confine ourselves to those elements and compounds which are employed in pharmacy, in the arts and manufactures, viz.

I. Bases.

Potassa, Soda, Ammonia, Baryta, Strontia, Lime, Magnesia, Alumina, Oxide of Chromium, Oxide of Zinc, Protoxide of Manganese, Protoxide of Cobalt, Protoxide of Nickel, Protoxide of Iron, Peroxide of Iron, Oxide of Cadmium, Oxide of Lead, Oxide of Bismuth, Oxide of Copper, Oxide of Silver, Protoxide

*of Mercury, Peroxide of Mercury, Peroxide of Platinum, Per-
oxide of Gold, Protoxide of Tin, Peroxide of Tin, Oxide of
Antimony.*

II. ACIDS.

· *Sulphuric Acid, Nitric Acid, Phosphoric Acid, Arsenious Acid,
Arsenic Acid, Boracic Acid, Carbonic Acid, Chromic Acid,
Chloric Acid, Silicic Acid, Oxalic Acid, Tartaric Acid, Para-
tartaric or Racemic Acid, Citric Acid, Malic Acid, Benzoic
Acid, Succinic Acid, Acetic Acid, Formic Acid.*

III. SALT-RADICALS AND NON-METALLIC ELEMENTS.

*Chlorine, Iodine, Bromine, Cyanogen, Fluorine, Sulphur,
Carbon.*

The subject of qualitative analysis is most properly divided into
four principal parts; viz.

1. THE ANALYTICAL OPERATIONS.
2. THE REAGENTS AND THE MODE OF THEIR APPLICATION.
3. THE DEPORTMENT OF VARIOUS BODIES WITH REAGENTS.
4. THE SYSTEMATIC COURSE AND METHOD OF QUALITATIVE
ANALYSIS.

It will now be readily understood that the pursuit of chemical
analysis requires practical skill and ability, as well as theoretical
knowledge; and that, consequently, a mere speculative study of
it can be as little expected to lead to success as purely empirical
experiments. To render the desired end attainable, theory and
practice must be combined.

CHAPTER I.

OPERATIONS.

§ 1.

THE operations of analytical chemistry are essentially the same as those of synthetical chemistry, although modified, of course, to a certain extent, according to the object we have in view, and the quantities which we have to operate upon, in analytical investigations.

The following are the principal operations occurring in qualitative analysis.

§ 2.

1. SOLUTION.

The term "*solution*," in its widest sense, is applied to the perfect union of a fluid with any substance, no matter whether gaseous, liquid, or solid. But we call solution more properly *absorption* when the dissolved substance is *gaseous*; and when *liquid*, the term *mixture* is more frequently made use of. The application of the term solution, in its usual and more restricted sense, is confined to the perfect union of a *solid* substance with a fluid.

The more minutely we divide any substance to be dissolved, the more we facilitate its solution. The liquid, by means of which solution is effected, is called the *solvent*. We term the solution *chemical*, if the solvent enters into chemical combination with the substance dissolved, *simple*, if no definite combination takes place.

In a *simple* solution, the dissolved body exists in a free state, and possessed of all its original properties, except those dependent on its form and cohesion ; it separates unaltered, when the solvent is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt in this case imparts its peculiar taste to the water, and on evaporating the latter, we re-obtain common salt in its original form. A simple solution is called *saturated*, when the solvent has received as much as it can hold of the dissolved substance. But as fluids dissolve generally larger quantities of a substance, the higher their temperature, the term *saturated*, as applied to *simple* solutions, is only relative, and refers invariably to a certain temperature. It may be laid down as a general rule, that elevation of temperature facilitates and accelerates simple solution.

A *chemical* solution contains the substance dissolved, not in the same state, nor possessed of the same properties as before ; the dissolved body is no longer free, but intimately combined with the solvent, the latter has also lost its original properties ; a new substance has thus been produced, and the solution manifests therefore now the properties of this new substance. A chemical solution also may be *accelerated* by elevation of temperature, and this is indeed usually the case, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same, in proportion to a given quantity of the solvent, whatever may be the difference of temperature—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature.

The reason of this is, that in chemical solution, the solvent and the body upon which it acts have invariably opposite properties, which they strive mutually to neutralize. Further solution ceases as soon as this tendency of mutual neutralization is satisfied. The solution is in this case said to be saturated, or more properly *neutralized*, and the point which denotes it to be so, is termed the point of saturation or neutralization. The most familiar illustration of this is found in the acids and alkalies or bases. Such substances require, in the first place, to be converted to the fluid state by means of a simple solvent. When the

opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present : e. g. when an aqueous solution of acetic acid is brought into contact with oxide of lead, there ensues, first, a chemical combination of the acid with the oxide, and finally a simple solution of the thereby produced acetate of lead in the water of the menstruum.

Crystallization and precipitation are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to the solid state. As both depend on the same cause, viz., on the absence of a solvent, it is impossible to assign exact limits to either ; in many cases they merge into one another. We must, however, consider them separately here, since they differ essentially in their extreme forms ; and, moreover, since the special objects which we purpose to attain by their application are, in most cases, very distinct.

§ 3

2. CRYSTALLIZATION.

We understand by the term crystallization, in a more general sense, every operation, or process, whereby bodies are induced to pass from the fluid to the solid state, and to assume certain regular, determinate, geometrical figures. But, as these figures, which we call *crystals*, are the more regular, and consequently the more perfect, the more slowly the operation is carried on, we always connect with the term " crystallization," the accessory idea of a *slow* separation,—of a *gradual* conversion to the solid state. The formation of crystals depends on the regular arrangements of the ultimate constituent particles of bodies (*molecules* or *atoms*) ; it can only take place, therefore, if these atoms possess perfect freedom of motion, and thus, in general, only when a substance passes from the fluid or gaseous to the solid state. Those cases, in which crystallization is induced by the simple fusion, or softening of a solid body, are to be considered as exceptions,—thus, for

instance, barley-sugar becomes white and opaque (crystallized) when moistened.

To induce crystallization, we have to remove the causes of the fluid or gaseous form of a substance. These causes are, either *heat alone,* e. g. in fused metals, or *solvents alone,* as in an aqueous solution of common salt; or *both combined,* as in a hot and saturated aqueous solution of nitrate of potass. In the first case, we obtain crystals by cooling the fused mass ; in the second, by evaporating the menstruum ; and in the third by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquors which remain after the separation of the crystals, are called *mother waters,* or *mother liquors.* The term *amorphous* is applied to such solid bodies as have no crystalline form.

We induce crystallization generally, either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same menstruum.

§ 4.

3. PRECIPITATION.

This operation differs from crystallization inasmuch as in precipitation the dissolved substance is converted to the solid state, not in a slow and gradual manner, but *suddenly ;* it is a matter of perfect indifference, as regards the application of the term precipitation to the process, whether this substance is crystalline or amorphous, whether it gravitates to the bottom of the vessel, or ascends or remains suspended in the liquid. Precipitation is caused either by modification of the solvent—thus sulphate of lime (gypsum) separates immediately from its solution in water upon the addition of alcohol—or it ensues in consequence of the separation of an educt insoluble in the menstruum ; thus, when ammonia is added to a solution of sulphate of alumina, the latter salt is decomposed, and the alumina, not being soluble in water, precipitates. Precipitation takes place also when, by the action of simple or double chemical affinity, new combinations ensue which are insoluble in the menstruum ; thus, oxalate of lime precipitates upon adding

oxalic acid to a solution of acetate of lime,—chromate of lead
upon mixing chromate of potash with nitrate of lead. In decom-
positions of this kind, induced by simple, or double affinity, one of
the new compounds remains generally in solution, and the same
is sometimes the case with the educt,—thus in the instances just
mentioned, the sulphate of ammonia, the acetic acid, and the
nitrate of potass, remain in solution. It may, however, happen
also that both product and educt, or the two products, precipitate,
and that nothing remains in solution; this is the case, for in-
stance, when a solution of sulphate of magnesia is mixed with
water of barytes; or a solution of sulphate of silver with chloride
of barium.

Precipitation is applied for the same purposes as crystallization,
viz. either to obtain a substance in the solid form, or to separate
it from other substances dissolved in the same menstruum. But
in qualitative analysis we resort to this operation more particularly
for the purpose of detecting and distinguishing substances by the
color, properties, and general deportment, which they exhibit when
precipitated, either in an isolated state, or combined with other
substances. The solid body separated by this process, is called
the *precipitate*, and the substance, which acts as the immediate
cause of its separation, is termed the *precipitant*. For the sake
of a more particular designation, we apply various terms to pre-
cipitates, according to their different nature; thus we distinguish
crystalline, pulverulent, flocculent, curdy, gelatinous precipitates,
&c. &c.

The terms *turbid, turbidity*, are made use of to designate the
state of a fluid which contains a precipitate so finely divided and
so inconsiderable in amount, that the suspended particles, although
impairing the transparency of the fluid, yet cannot be clearly dis-
tinguished. We may generally promote the separation of a
precipitate by strongly agitating the menstruum, and also by
elevating its temperature. The vessels used for the purpose of
precipitation should therefore, if possible, admit of both these
operations. In qualitative analysis we employ principally tubes
of thin glass, closed at the bottom, such as are usually called test-
tubes, (§ 14. 8.); these enable us, moreover, to operate upon very

minute quantities, to inspect the whole process, and to observe the colour of liquids and precipitates.

The two operations described at § 5 and 6, viz. *filtration* and *decantation*, serve to effect the mechanical separation of fluids from matter suspended therein.

§ 5.

4. FILTRATION.

This operation consists simply in passing the fluid from which we wish to remove the mechanically-suspended solid particles, through a filtering apparatus, formed usually by a properly-arranged piece of unsized paper, supported by a funnel; an apparatus of this description allows the fluid to trickle through with ease, whilst it retains the solid particles completely. We employ smooth filters and plaited filters : the former, in cases where the defiltrated solid substance is to be made use of; the latter, when we merely wish to clear the solution. Smooth filters are prepared by double folding of a circular piece of paper in such a manner, that the folds form right angles. The preparation of plaited filters is more properly a matter for ocular demonstration than for description. In very precise operations, the filters must not project over the brim of the funnel. It is in most cases advisable to moisten the filter previously to passing the fluid through it; since this not only tends to accelerate the process, but it renders the solid particles less liable to pass through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially from iron and lime. It is advisable always to keep two kinds, one of greater density for the separation of very finely-divided precipitates, and one of greater porosity for the speedy separation of grosser particles. In order to obtain exact results it is necessary to use filtering paper which has been washed, first with dilute hydrochloric acid, and afterwards with distilled water. The funnels must be either of glass or of porcelain. (§ 14, 11.)

§ 6.

5. DECANTATION.

This operation is frequently resorted to instead of filtration, when the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; since, in that case, they will speedily subside to the bottom, rendering it easy, either to decaut the supernatant liquid by simply inclining the vessel, or to remove it by means of a syphon.

In cases where filtration or decantation are applied for the purpose of obtaining the solid substance, the latter must be freed, subsequently, by repeated *washing* from the liquid still adhering to it. This operation is also termed *edulcoration*. The washing of precipitates collected in a filter is usually effected by means of a washing bottle, such as is represented by Figure 1.

FIG. 1.   FIG. 2.
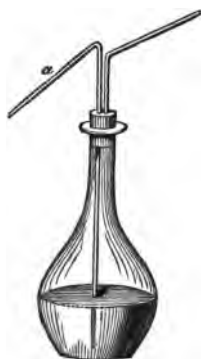
The washing bottle, Fig. 1, consists of a flask, closed with a perforated cork, into which is adapted a small glass tube, drawn out to a fine point at the top (*a*). If air be blown into the flask through this tube, and, when the air is sufficiently compressed, the flask be reversed, so as to immerse the inner aperture of the tube in the water, a fine jet of water will be expelled with a certain degree of force; this contrivance is admirably adapted for

washing precipitates.—Fig. 2, represents a bottle of a different
construction; this may also be used to wash precipitates with
boiling water; it affords, moreover, this advantage, that it en-
ables the operator to produce a continual stream of water. The
engraving needs no explanation,—the tube *a* is drawn out *into a
fine point* at its anterior aperture.

There are four operations which serve to separate volatile sub-
stances from less volatile, or from fixed bodies, viz. EVAPORATION,
DISTILLATION, IGNITION, and SUBLIMATION. The two former of
these operations are applied exclusively to fluids, the two latter
exclusively to solids.

<center>§ 7.</center>

<center>6. EVAPORATION.</center>

This operation is of very frequent occurrence. It serves to
separate volatile fluids from less volatile, or from fixed bodies,
(no matter whether solid or fluid,) in cases where the residuary
substance alone is of importance, whilst the evaporating matter is
entirely disregarded ;—thus, for instance, we have recourse to eva-
poration for the purpose of removing from a saline solution part
of the water, in order to induce the salt to crystallize; we resort
to this process also for the purpose of removing the whole of the
water of the menstruum from the solution of a non-crystalline
substance, so as to obtain the latter in a solid form, &c. &c.
The evaporated water is entirely disregarded in either of these
cases, and the only object in view is, to obtain, in the former
case, a more concentrated fluid, and, in the latter, a dry sub-
stance. These objects are invariably attained by converting the
fluid which is to be removed into the gaseous state; and this ge-
nerally by the application of heat; sometimes, also, by leaving the
fluid for a certain time in contact with the atmosphere, or with
confined air, which is constantly kept dry by hygroscopic sub-
stances; or, finally, in many cases, by placing the fluid in rarified
air, with the simultaneous application of hygroscopic substances,
The process of heating is conducted either over an open fire, (as
coal-fire or flame of spirits of wine,) or in the sand-bath, or by
means of steam, (in the water-bath,) &c. &c. Concentrated sul-

<center>6</center>

phuric acid, quick lime, and chloride of calcium, are the cheapest and most efficient hygroscopic substances. The vessels used in evaporation are made of porcelain, glass, platinum, or silver, and have usually the shape of a dish or shallow basin.

§ 8.

7. DISTILLATION.

This operation serves to separate a volatile liquid from a less volatile or fixed substance, (no matter whether solid or fluid,) and subsequently to recover the evaporated fluid. In order to attain this object, it is necessary to reconvert the liquid from the gaseous form in which it evaporates into the fluid state. A distilling apparatus consists, consequently, of three parts, no matter whether admitting of separation or not. These three parts are—1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapor ; 2nd, an apparatus in which this vapor is cooled again or *condensed,* and thus reconverted to the fluid state ; and 3rd, a vessel which receives the thus reproduced fluid (the distillate). In distillation on a small scale, we employ generally small glass retorts and receivers, but for the distillation of large quantities, we use either a metallic apparatus,—a copper still with helmet, and condensing-tube of tin or pewter,—or large glass retorts.

§ 9.

8. IGNITION.

Ignition is, in a certain measure, for solid bodies, what evaporation is with regard to fluids ; since it serves (at least generally) to separate volatile substances from less volatile, or from fixed bodies, in cases where the residuary substance alone is of importance. Ignition always requires the application of a high temperature, and in this it differs from exsiccation. The form or state which the eliminated substance assumes on cooling, is a matter of perfect indifference as to the term we apply to the operation.

The elimination of a volatile substance is the most frequent purpose of ignition. In some instances, however, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place ; thus the oxide of chromium is

converted by ignition into its insoluble modification, &c. &c,—
Crucibles are the vessels made use of in ignition. In analytical
experiments we select, according to the substance to be ignited,
either porcelain, platinum, or silver crucibles. In operations on
a large scale, we use either hessian or black-lead crucibles. The
necessary heat is derived either from a charcoal or coke-fire or, in
experiments on a small scale, from a BERZELIUS' spirit-lamp or
a gas-lamp.

§ 10.

9. SUBLIMATION.

The term *sublimation* designates that process which serves to
expand solid bodies into vapor, by the application of heat, and
subsequently to recondense the vapor to the solid state, by refri-
geration :—the substance thus volatilized and recondensed is
called a *sublimate.* Sublimation is consequently a *distillation of
solid bodies.* We have recourse to this process mostly to effect
the separation of substances possessed of different degrees of vola-
tility. Its application is of the highest importance in analysis for
the detection of several substances, e. g. of arsenic. The vessels
used in sublimation are of various shapes, according to the dif-
ferent degrees of volatility of the substances we have to operate
upon. In sublimation for analytical purpose we employ generally
glass tubes closed at both ends.

§ 11.

10. FUSION AND FLUXING.

We designate by the term " fusion," the conversion of a solid
substance into a fluid form, by the application of heat ; fusion is
most frequently resorted to for the purpose of effecting the com-
bination or the decomposition of bodies. The term " fluxing" is
applied to this process in cases where substances, either altogether
insoluble, or very difficult of solution in water and acids, are, by
fusion, in conjunction with some other body, modified or decom-
posed in such a manner, that they, or the new-formed compounds,
subsequently admit of solution in water or acids. Fusion and
fluxing are conducted either in porcelain, silver, or platinum cru-

cibles, according to the nature of the analysed compound. Should a BERZELIUS' spirit-lamp, or a gas-lamp, fail to produce the necessary degree of heat, the crucible containing the mixture intended for fusion, is to be introduced into a larger hessian, and the latter exposed to a charcoal or coke fire.

The application of fluxing is especially required for the analysis of the sulphates of the alkaline earths, and also for that of many silicates. The flux most commonly used is carbonate of soda, or carbonate of potassa, or, better still, a mixture of both, in equal atomic proportions, (vide § 76). In certain cases, hydrate of barytes is used instead of the alkaline carbonates, (vide § 77). But in either case the operation is conducted in platinum crucibles.

I have to add here, a few precautionary rules for the prevention of damage to the platinum vessels used in these operations. No substance, evolving chlorine, ought to be treated in platinum vessels ; no nitrate of potassa, caustic potassa, metals, sulphurets, or alkaline cyanides, should be fused in such vessels, nor ought readily deoxidizable metallic oxides, organic metallic salts, or phosphates, to be ignited in them in the presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them directly to an intense charcoal fire, since the action of the ashes, under such circumstances, gives readily rise to the formation of silicide of platinum, which renders the vessel brittle.

I have still to mention, in this place, the following operation, which bears some affinity to fusion.

§ 12.

11. DEFLAGRATION.

We understand by the term "*deflagration*," in a more extended sense, every process of decomposition attended with noise or detonation,—(the *cause* of the decomposition is a matter of perfect indifference as regards the application of the term in this sense).

We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another admixed substance—(usually of

a nitrate or chlorate,) and connect with it the idea of sudden
and violent combustion, attended with vivid ignition and noise or
detonation. Deflagration is resorted to either to produce a cer-
tain oxide,—thus sulphuret of arsenic is deflagrated with nitrate
of potassa to obtain arseniate of potassa ;—or it is applied to prove
the presence or absence of a certain substance,—thus salts are
tested for nitric or chloric acid by fusing them in conjunction
with cyanide of potassium, and observing whether this process
will cause deflagration or not, &c. &c.

To attain the former object, the perfectly dry mixture of the sub-
stance under examination and of the deflagrating agent, is to be
projected, in small portions, into a red-hot crucible. Experiments
of the latter description are invariably made upon very minute
quantities ; the process is, in such cases, best conducted on a
piece of thin platinum plate, or in a small spoon.

§ 13.

12. THE USE OF THE BLOW-PIPE.

This operation belongs exclusively to the province of analytical
chemistry, and is of paramount importance in many analytical
processes. We have to examine here, 1, the apparatus ; 2, the
mode of its application ; and 3, the results of the operation.

The blow-pipe is a small instrument, usually, made of brass.
It was originally used by metallurgists for the purpose of solder-
ing, whence it derived the name of "soldering pipe"—*Löthrohr*—
by which the Germans designate it. It consists of three distinct
parts; viz. 1st, a tube through which air is blown from the mouth;
2nd, a small vessel into which this tube is ground air-tight,—
(this vessel serves to collect and retain the moisture of the air
blown into the tube ;)—and 3rd, a smaller tube, which is likewise
closely fitted into this vessel, and forms a right angle with the
large tube ; this small tube has a very fine aperture at its anterior
extremity. (§ 14. 4.) The blow-pipe serves to conduct a fine
and continuous stream of air into the flame of a candle or lamp.
Such a flame presents, under ordinary circumstances, three dis-
tinct parts to the eye ; viz. 1st, a dark nucleus in the centre;
2nd, a luminous part surrounding this nucleus ; and 3rd, a kind

of mantle encircling the whole flame, and but feebly luminous. The dark nucleus is formed by the gases which the heat evolves from the fuel; these gases cannot burn here, owing to want of oxygen. In the luminous sphere they come into contact with a certain amount of oxygen, although insufficient for their complete combustion. The hydrogen of the carburetted hydrogen gases evolved, burns therefore principally here, whilst the carbon separates in a state of intense white heat, causing thus the luminousness of this part   In the outer coat, the access of air is no longer limited, and all the gases, not yet burned, are consumed. This part of the flame is the hottest. Oxidizable bodies oxidize, therefore, with the greatest possible rapidity, when placed in it, since all the conditions of oxidation are here united, viz. high temperature, and an unlimited supply of oxygen. This part of the flame is accordingly called the *oxidizing flame*.

On the other hand, oxides having a tendency to yield up their oxygen, suffer *reduction*, when placed within the *luminous* part of the flame, the oxygen being withdrawn from them by the carbon and the still unconsumed carburetted hydrogen present in this sphere. The luminous part of the flame is therefore called the *reducing flame*.

Now, if we conduct a fine stream of air into a flame, we have oxygen, not merely around the outer, but also in the inner part. Combustion takes place, therefore, in both parts. But this stream of air rushing with a certain force into the flame, carries forward the gases evolved, mixes intimately with them, and effects their combustion at a certain distance from the aperture of the blow-pipe. This point, which is marked by a bluish light, is the hottest part of the whole flame, since the intimate intermixture of the air with the gases favors here the most complete combustion. The luminous part of the flame being thus surrounded on both sides by very hot flames, acquires likewise an extraordinary increase of heat; this elevation of temperature forms the principal object which we intend to attain by the application of the blow-pipe. The hottest part of the flame lies now, of course, somewhat beyond the apex of the inner nucleus. In a reducing flame of this description many bodies will fuse readily, which a common flame

C

would fail to effect. The heat of the oxidizing flame also is considerably increased by the blow-pipe being more strongly concentrated upon one point.

For *fuel* we use either an oil-lamp, a wax candle, or a lamp fed with a solution of oil of turpentine in spirits of wine. A common spirit-lamp does not always produce the necessary degree of heat.

The *current* is to be produced with the cheek-muscles alone, and not with the lungs. The way of effecting this may be readily acquired by practising for some time to breathe calmly, with puffed-up cheeks, and whilst holding the blow-pipe between the lips ; a little practice and patience will soon enable the student to produce a continuous, even, and steady current.

The *supports* on which the substances to be examined are exposed to the blow-pipe flame, are generally either wood, charcoal, or platinum wire or plate. In the choice of charcoal intended for blow-pipe experiments, we have to look more particularly to the coal being thoroughly charred, otherwise, it will split and throw off the substances placed on it, (vide § 79.) The substances to be examined are put into small conical cavities scooped with a penknife, or with a little tin tube. We generally employ charcoal as a support, when we want to reduce a metallic oxide, or to ascertain the degree of fusibility of a substance.

Metals which are volatile at the heat of the ordinary flame, evaporate wholly, or in part, upon the reduction of their oxides. But these metallic vapors are reoxidized in passing through the outer flame, and the oxide thus produced forms a slight incrustation around the substance upon the charcoal. Many of these incrustations exhibit characteristic colors which serve to assist in the detection of the metals.

The platinum wire, as well as the platinum plate, should be selected rather thin. (Vide § 14, 6 and 7.) We make use of platinum wire generally when fusing bodies in conjunction with fluxes, (vide § 82 and 83,) for the purpose of inferring their nature from the color and other properties of the button produced.

What renders the application of the blow-pipe particularly

useful in chemical experiments, is the great facility with which the intended results are attained. The results are of a twofold kind, viz. either they afford us simply an insight into the general properties of the examined body, and enable us accordingly only to determine the *class* to which it belongs, i. e. whether it is fixed, volatile, fusible, &c. &c.; or the phenomena which we observe enable us at once to recognise the particular body which we have before us. We shall have occasion to describe these phenomena when treating of the deportment of the individual substances with reagents.

APPENDIX TO THE FIRST CHAPTER.

§ 14.

APPARATUS AND UTENSILS.

As the student cannot well be supposed to be acquainted with the apparatus, &c. &c. necessary for the processes of chemical analysis,—I deem it advisable to furnish him here with a list of those articles which are required for the performance of simple experiments and investigations. I shall at the same time point out the principal qualities which these articles should possess.

1. A BERZELIUS SPIRIT-LAMP.* The vessel containing the spirit of wine should be connected with the wick-holder by means of a narrow tube, to avoid explosions;—the chimney should not be too narrow. The aperture through which the spirit of wine is poured should not be air-tight

2. A LAMP-STAND with moveable rings and brackets.

3. A GLASS SPIRIT-LAMP with ground cover and brass wick-tube.

4. A BRASS BLOW-PIPE with a mouth-piece made of horn or bone, (vide § 13.) The principal tube may be about seven inches in

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* The application of gas for innumerable purposes in analytical chemistry in this country, deserves a passing notice here.

length, slightly varying, of course, according to the visual distance of the individual ; the length of the smaller tube ought to be about two inches.   Both must be ground air-tight into the small vessel, which, as I have already stated at § 13, is intended to collect and retain the moisture of the air blown through the pipe.   It is advisable to keep two small tubes at hand, one with a wider, and the other with a narrower opening.—Most of the small tubes usually sold at the chemical instrument makers' are fitted simply with a small perforated platinum plate at their aperture.   Those, however, which are provided with a finely perforated platinum cap are more durable ; whenever the jet of these caps happens to be stopped up, the obstruction may be at once removed by igniting the cap before the blow-pipe.

5. A PLATINUM CRUCIBLE with ground cover ; this should not be too deep, in proportion to its breadth.

6. A PLATINUM SPATULA, about two inches long and one inch in breadth ; this should be of sufficient thickness, and as clean and smooth as possible.

7. A FEW PIECES OF PLATINUM WIRE, of the size of lute-strings, varying in length from three to four inches, and twisted at both ends into a small loop.   It is advisable to keep these wires in a small phial filled with water, since most of the buttons produced by fusion or fluxing dissolve in water ; by this means the wires may be kept always clean.

8. A STAND WITH FROM TWELVE TO TWENTY TEST TUBES.   The latter may vary from four to six or eight inches in length, and must be of different width.   They should be made of thin white glass, and so well annealed, that they do not crack even though boiling water be poured into them.   Their brim must be quite round, and slightly turned over ; it ought to have no lip, since the latter is of no use, and prevents the tube from being closely stopped with the finger.

9. SEVERAL BEAKER GLASSES AND SMALL RETORTS of thin, well-annealed glass.

10. SEVERAL PORCELAIN EVAPORATING DISHES, AND A VARIETY OF SMALL PORCELAIN CRUCIBLES.   Those of the royal manufacture of Berlin are unexceptionable, both in shape and durability.

11. SEVERAL GLASS FUNNELS of various sizes. They must be inclined at an angle of sixty degrees, and onght to merge into their tube at a definite angle.

12. A WASHING BOTTLE, capable of holding from twelve to sixteen ounces of water, (vide § 6.)

13. SEVERAL GLASS RODS AND TUBES. The latter may be bent, drawn out, &c., over a Berzelius spirit lamp.

14. A selection of WATCH-GLASSES.

15. A small AGATE MORTAR.

16. Several small IRON SPOONS.

17. A pair of small PINCERS, with scissor-handles, the blades joining close together, and bent at their extremity at a right or slightly obtuse angle.

These should be varnished.

CHAPTER II.

REAGENTS.

§ 15.

VARIOUS phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases liquids change their color, in others precipitates are formed, sometimes effervescence takes place, and sometimes deflagration, &c. Now, if these phenomena are very striking, and attendant only upon the combination or decomposition of two definite bodies, it is obvious that the presence of one of these bodies may be detected by means of the other: e. g. if we know that a white precipitate, of certain definite properties, is formed upon mixing baryta with sulphuric acid, it is clear that, if by adding baryta to any liquid we obtain a precipitate exhibiting these properties, we may conclude that this liquid contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena, are called *reagents*.

These are divided into *general* and *special* reagents, according to the object attained by their application. By *general* reagents, we understand those which serve to determine the *class* or *group* to which the substance under examination belongs; and by *special* reagents those which serve to detect *individual* substances. That the limits between these two divisions cannot be drawn with any degree of precision, ought not to be considered a valid objection to this classification, which is simply intended to accustom the student to keep invariably in mind whether he purposes to ascertain the *group* to which the substance under examination belongs, or to determine the latter *individually*.

The terms *characteristic* and *susceptible* are made use of to designate the two principal properties upon which the greater or less utility of a reagent depends. We call a reagent *characteristic*, if the alteration attendant upon the detection of the substance tested

for, is so distinctly marked as to admit of no mistake. Thus, iron
is a characteristic reagent for copper, protochloride of tin for mer-
cury, because the phenomena produced by these reagents, viz. the
separation of metallic copper and of globules of mercury, admit of
no mistake. We call a reagent *susceptible*, if its action is clearly
perceptible, although but a very small quantity of the substance
tested for be present, such is for instance the action of starch upon
iodine. A great many reagents are *both* characteristic and suscep-
tible: thus, for instance, perchloride of gold for protoxide of tin, ferro-
cyanide of potassium for copper, and for peroxide of iron, &c. &c.

I need scarcely mention that reagents must in general be
chemically pure, i. e. they must contain no extraneous sub-
stance in admixture, since, if this be not the case, their indica-
tions cannot be relied upon. We must therefore make it an inva-
riable rule to *test the purity of reagents before we use them,* no
matter whether they be articles of our own production or of pur-
chase. The instructions which I shall give in this respect when
treating of the various reagents individually, refer, of course, only
to such contaminations as are likely to arise from the mode of
their respective preparation, but not to accidental admixtures.

One of the most common sources of error in qualitative ana-
lysis proceeds from missing the proper measure—the right quan-
tity—in the application of reagents. Such terms as " *addition in
excess,*" " *supersaturation,*" &c., often induce novices to suppose
that they cannot add *too* much of the reagent, and thus some will
fill a test tube with acid simply to supersaturate a few drops
of an alkaline fluid, whereas every drop of acid added, after
the neutralization point has once been reached, is to be looked
upon as an *excess* of acid. On the other hand, the addi-
tion of an insufficient amount is to be equally avoided, since a
reagent, when added in insufficient quantity, often produces phe-
nomena quite different from those which will appear if the same
reagent be added in excess : e. g. a solution of perchloride of mer-
cury yields a *white* precipitate, when tested with a *small* quantity
of sulphuretted hydrogen ; but when treated with sulphuretted
hydrogen *in excess*, the precipitate is *black*. Experience has,
however, proved that the most common mistake beginners are

liable to is, to add the reagents too copiously. The reason why this over-addition must impair the accuracy of the results, is obvious; we need simply bear in mind, that the changes effected by reagents, are perceptible within certain limits only, and that accordingly they may be the more readily overlooked the nearer we approach these limits by diluting the fluid.

No special and definite rules can be given for avoiding this source of error; a general rule may, however, be laid down, and even this may be considered sufficient, to point out the proper measure in all, or at least in most cases. It is simply this: *let the student always reflect, before the addition of a reagent, for what purpose he applies it, and what are the phenomena he intends to produce.*

We divide reagents into two classes, according as the state of fluidity which is indispensable for the manifestation of the action of reagents upon the various bodies, is induced by the application of heat, or by means of liquid solvents; we have accordingly, 1, *Reagents in the humid way;* and 2, *Reagents in the dry way.* For greater clearness and simplicity, we subdivide these two principal classes as follows:—

A. REAGENTS IN THE HUMID WAY.

I. GENERAL REAGENTS.

a. *Reagents principally used as* SIMPLE SOLVENTS.

b. *Reagents principally used as* CHEMICAL SOLVENTS.

c. *Reagents which serve principally to separate, or otherwise to characterise groups of substances.*

II. SPECIAL REAGENTS.

a. *Reagents which serve principally for the detection of the* BASES.

b. *Reagents which serve principally for the detection of the* ACIDS.

B. REAGENTS IN THE DRY WAY.

I. FLUXES.

II. BLOW-PIPE REAGENTS.

A. REAGENTS IN THE HUMID WAY.

I. General Reagents.

a. Reagents principally used as simple solvents.

§ 16.

1. WATER.   (H O).

Preparation.—Pure water is obtained by distilling spring-water from a copper-still, or from a glass retort. This distillation should not be carried beyond three-fourths of the quantity operated upon. Rain water collected in the open air may in many cases be substituted for distilled water.

Tests.—Pure distilled water must leave no residue upon evaporation, nor should it alter the color of Georgina paper. (Vide § 24, 1. γ.)   Nitrate of silver, chloride of barium, oxalate of ammonia, and lime-water, must not impair its transparency.

Uses.—We use water* principally as a simple solvent for a great variety of substances. It serves moreover to effect the transformation of several neutral metallic salts into soluble acid, and insoluble basic compounds; this is the case particularly with chloride of antimony and with the salts of bismuth.

§ 17.

2. ALCOHOL. $(C_4 H_6 O_2 = Ae O, H O)$.

Preparation.—Two sorts of alcohol are used in chemical analyses; viz. 1st, spirits of wine of 0·83 or 0·84 spec. gr. (*spiritus vini rectificatus* of the shops;) and 2nd, absolute alcohol. The latter may be prepared by distilling the former from fused chloride of calcium, or by mixing with anhydrous sulphate of copper, pouring off the solution, and redistilling.

Tests.—Pure alcohol must completely volatilize, and ought not to cause the slightest smell of fusel oil, when rubbed between the hands; nor should it redden litmus paper.

* In chemical experiments we use *exclusively* distilled water; whenever therefore the term "water" occurs in the present work, distilled water is meant.

Uses.—Many substances are soluble in alcohol, whilst others are insoluble in this menstruum. Alcohol is therefore frequently employed to effect the separation of the former from the latter, thus, for instance, to separate chloride of strontium from chloride of barium. Alcohol serves likewise to precipitate from aqueous solutions such substances as are insoluble in it, e. g. to precipitate malate of lime. We use alcohol, moreover, for the production of various kinds of ether, (especially of acetic ether, which is particularly characterized by its agreeable odor;) and likewise to co-operate with acids in the reduction of certain substances, for instance, of peroxide of lead, chromic acid, &c. &c. Alcohol serves also for the detection of various substances which impart a characteristic tint to its flame; such are especially boracic acid, strontia, soda, and potassa.

§ 18.

3. ETHER.　$(C_4 H_5 O = Ae O)$.

Ether finds but very limited application in the analysis of inorganic bodies. It serves, in fact, almost exclusively to detect and isolate bromine, (§ 101, *b*,) and for this purpose the officinal ether of commerce is sufficiently pure and strong.

b. Reagents which are principally used as chemical solvents.

§ 19.

1. HYDROCHLORIC ACID.　(H Cl).

Preparation.—Pour a cooled mixture of 13½ parts of sulphuric acid with four parts of water, over eight parts of chloride of sodium in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath, until the evolution of gas ceases; conduct the evolved gas, by means of a double-limbed tube, into a flask containing twelve parts of water, and take care to keep this receiver constantly cool. To prevent the gas from receding, the tube ought only to dip about one line into the water of the receiver. Should the sulphuric acid employed in the process contain nitric acid, the gas which passes over first, (and which in that case contains chlorine,) must be received separately. The hydro-

chloric acid produced is to be diluted with water until its specific
gravity is from 1·11 to 1·12.

Tests.—Hydrochloric acid, intended for the purposes of che-
mical analysis, must be perfectly colorless, and leave no residue
upon evaporation; it should not discolor indigo-solution upon
ebullition. Chloride of barium ought not to produce any precipi-
tate, either in the highly diluted acid, (sulphuric acid,) nor even
after ebullition with nitric acid, (sulphurous acid). Sulphuretted
hydrogen must leave it unaltered. After neutralization with am-
monia, and subsequent addition of a slight excess of acetic acid,
ferrocyanide of potassium must not produce any precipitate in it,
nor even impart to it the slightest tinge of blue.

Uses.—Hydrochloric acid serves as a solvent for a great many
substances. It dissolves oxides and peroxides in the form of
chlorides, the solution being, in the latter case, mostly attended
with liberation of chlorine.—Salts, with insoluble or volatile acids,
are also converted by hydrochloric acid into chlorides, with sepa-
ration of the original acid; thus carbonate of lime is converted
into chloride of calcium, with liberation of carbonic acid. Hy-
drochloric acid dissolves salts with non-volatile and soluble acids,
apparently without decomposing them, (e. g. phosphate of lime);
but we must suppose that solutions of this description arise from
the formation of a soluble chloride and of a soluble acid salt of the
acid of the dissolved compound; thus, for instance, in the case of
phosphate of lime, we must assume that chloride of calcium and acid
phosphate of lime are formed. This explanation, however, will
not serve for salts with such acids as form no soluble acid com-
pound with the base present; in such cases we must assume,
either that the acid of the dissolved salt is present in the solution,
in a free state, (borate of lime,) or that the hydrochloric acid acts
really as a *simple* solvent. (Compare § 2.) Hydrochloric acid is
also applied as a *special* reagent for the detection and separation
of oxide of silver, protoxide of mercury, and lead, (vide infra,)
and likewise for the detection of free ammonia (with which it pro-
duces dense white fumes of sal ammoniac in the air).

$$\S\ 20. \quad H\,N\,O_3$$
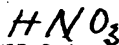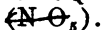
2. NITRIC ACID. $(N\,O_5)$.

Preparation.—It is seldom necessary to prepare nitric acid, as it may be readily obtained quite pure, but the nitric acid of commerce often contains sulphuric acid and hydrochloric acid. To free it from these admixtures, solution of nitrate of silver is to be added to it, as long as any precipitate of chloride of silver continues to form ; this precipitate is allowed to subside ; the supernatant fluid is decanted into a retort, and distilled to within a small fraction of its whole amount   The distillate is then, if necessary, diluted with water until the specific gravity of the diluted acid is equal to 1·2.

Tests.—Pure nitric acid must be colorless, and, when evaporated on a platinum plate, leave no residue.   The addition of solution of nitrate of baryta, or of nitrate of silver, must not cause the slightest turbidity.   It is advisable to dilute the acid with water before adding these reagents, otherwise nitrates will precipitate.

Uses.—Nitric acid serves, in the first place, as a chemical solvent for metals, oxides, sulphurets, oxygen salts, &c.   The way in which the nitric acid effects the solution of metals and sulphurets, is this : it oxidizes these bodies first, at the expense of part of its own oxygen, and transforms the produced oxides subsequently into nitrates.   Most oxides dissolve in nitric acid directly as nitrates, and the same is the case with most of the insoluble salts with weaker acids, the latter being expelled by the nitric acid in the process of solution.   Salts with soluble non-volatile acids are dissolved by nitric acid in the same manner as by hydrochloric acid. (Vide § 18)   Nitric acid serves moreover very frequently as an oxidizing agent ; thus it is used, for instance, to convert the protoxide of iron into the peroxide, to decompose hydriodic acid and the iodides, &c.

$$\S\ 21.$$

CHLORO-NITRIC ACID.   AQUA REGIA.

Preparation.—One measure of pure nitric acid is mixed with from three to four measures of pure hydrochloric acid.

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Nitric and hydrochloric acids decompose each other, forming, as shown by Gay Lussac, two compounds which are gaseous at the ordinary temperature, $N O_2 Cl_2$ and $N O_2 Cl$, at the same time water and free chlorine are eliminated. On adding $N O_5$ to three equivalents of H Cl we may assume that only hypochloro-nitric acid $N O_2 Cl_2$ with chlorine and water are formed, viz. $N O_5$ + 3 Cl H = $N O_2 Cl_2$ + Cl + 3 H O.

This dcomposition ceases when the fluid is saturated with the gases, but it recommences the instant that this state of saturation is disturbed by the application of heat, or the action of certain metals. The presence of free chlorine and the above-named acids renders aqua regia the most powerful solvent for metals, with the exception of those which form insoluble compounds with chlorine.—Aqua regia serves principally to effect the solution of gold and platinum, (which metals are insoluble both in hydrochloric and also in nitric acid,) and the decomposition of divers sulphurets, e. g. cinnabar, &c. &c.

§ 22. $H \, C_2 H_3 O_2$

4. ACETIC ACID. ($C_4 H_3 O_3$ = A).

Preparation.—Triturate ten parts of crystallized neutral acetate of lead, with three parts of effloresced sulphate of soda; introduce the powder into a retort, add a cooled mixture of two and a half parts of sulphuric acid with an equal weight of water, and distil to dryness in a sand-bath. The best way of connecting the receiver with the retort, is by means of a LIEBIG's condensing apparatus.

Tests.—Pure acetic acid must leave no residue upon evaporation. The diluted acid ought not to be precipitated by sulphuretted hydrogen, nor by solution of nitrate of silver or nitrate of baryta, by the latter not even after previous boiling with nitric acid. Should nitrate of baryta produce a precipitate in acetic acid which has been previously boiled with nitric acid, this is a proof of the presence of sulphurous acid; the acetic acid in such cases is to be digested with brown peroxide of lead, and subsequently redistilled. Pure acetic acid, moreover, must not decolor solution of indigo. (Vide § 102, *a*).

Uses.—Acetic acid possesses a greater solvent power for some substances than for others;—it is used, accordingly, to separate the former from the latter ; thus it serves, for instance, to distinguish oxalate of lime from phosphate of lime. We apply acetic acid also for the acidulation of fluids, in cases where we wish to avoid the use of mineral acids.

§ 23.

5. CHLORIDE OF AMMONIUM.   ($N H_4$, Cl).

Hydrochlorate of Ammonia.—Muriate of Ammonia.—Sal Ammoniac.

Preparation.—The sal ammoniac of commerce may generally be purified by simple recrystallization. Should it contain iron, this may be removed by the following process : a small portion of hydrosulphuret of ammonia is added to the solution of the sal ammoniac, and the precipitate which forms is allowed to subside ; the fluid is then filtered off, and hydrochloric acid added to the filtrate, until the latter acquires a feebly acid reaction ; the mixture is then heated to ebullition, filtered, saturated with ammonia, and finally crystallized. For use, one part of the salt is dissolved in eight parts of water.

Tests.—Solution of sal ammoniac, when evaporated on a platinum plate, should leave a residue, which must subsequently, upon continued application of heat, completely volatilize. It ought not to be affected by the action of hydrosulphuret of ammonia. Its reaction should be perfectly neutral.

Uses.—Sal ammoniac serves principally to retain certain oxides, (e. g. protoxide of manganese, magnesia,) or salts, e. g. tartrate of lime,) in solution, upon the precipitation of other oxides or salts by ammonia or some other reagent. This application of sal ammoniac is based upon the tendency of the ammoniacal salts to form double compounds with other salts. Sal ammoniac serves also to distinguish between precipitates possessed of similar properties, and thus, for instance, to distinguish the *basic phosphate of magnesia and ammonia* which is insoluble in sal ammoniac, from other precipitates of magnesia. We use sal ammoniac,

moreover, to precipitate, from potassa solutions, various substances which are soluble in potass, and insoluble in ammonia, for in-sance, alumina, oxide of chromium, &c. &c. In this process, the elements of the sal ammoniac transpose with those of the potassa, and this transposition results in the formation of chloride of potassium, water, and ammonia. Sal ammoniac is applied also as a *special* reagent for the precipitation of platinum as ammonio-chloride of platinum.

c. Reagents which serve principally to separate or otherwise to characterize groups of substances.

§ 24.

1. REAGENT PAPERS.

a. BLUE LITMUS PAPER.

Preparation.—One part of litmus of commerce is to be digested with six parts of water; the solution is subsequently to be filtered, and the intensely blue filtrate divided into two equal parts ;— the free alkali in the one part is then to be saturated by stirring with a glass rod which has been dipped previously into very dilute sulphuric acid, and repeating this process until the fluid begins to look red; the other part of the filtrate is now added to the reddened fluid, and the whole mixture poured out into a basin, where slips of fine unsized paper are finally drawn through it. These slips are afterwards suspended over threads, and left to dry. The color of litmus paper must be perfectly uniform, and neither too light nor too dark.

Uses.—Litmus paper serves to detect the presence of free acid in fluids, since acids change its blue color to red. It is to be borne in mind, however, that the neutral salts of most of the heavy metallic oxides produces the same effect.

β. REDDENED LITMUS PAPER.

Preparation.—Blue tincture of litmus is stirred with a glass rod dipped previously into dilute sulphuric acid, and this process repeated until the fluid begins to look distinctly red. Slips of

paper are then drawn through the tincture, and finally dried as at
α. The dried slips must look distinctly red.

Uses.—Pure alkalies, and alkaline earths, and the sulphurets
of these substances, restore the blue color of reddened litmus
paper ; alkaline carbonates and the soluble salts of several other
weak acids, especially of boracic acid, possess the same property.
This reagent serves therefore for the detection of these substances
in general.*

γ. GEORGINA PAPER.

Preparation.—The violet-coloured petals of *Georgina pur-
purea* (purple dahlia) are boiled in water or digested with
spirit of wine ; the fluid is filtered, and slips of paper are drawn
through the filtrate : the latter should be neither more nor less
concentrated than is necessary to make the paper, after drying,
appear of fine and rather light violet-blue color. Should the
color too much incline to red, this may be remedied by adding a
small amount of ammonia to the tincture.

Uses.—Georgina paper is reddened by acids, whilst alkalies
impart a beautiful green tint to it. It is therefore an extremely
convenient substitute both for the blue and the reddened litmus
paper. This reagent, if properly prepared, is extremely suscep-
tible for acids as well as for alkalies. Concentrated solutions of
caustic alkalies turn Georgina paper yellow, by destroying the
coloring matter.

δ. TURMERIC PAPER.

Preparation.—One part of bruised turmeric-root is digested
and heated with six parts of dilute spirit of wine ; the tincture
obtained by this process is filtered, and slips of fine paper are
dipped into it. The dried slips must exhibit a fine yellow tint.

Uses.—Turmeric paper serves, like reddened litmus paper and
Georgina paper, for the detection of free alkalies, &c. ; since they
change its yellow color to brown. It is not quite so susceptible
as the other reagent papers, but the change of color which it

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* Mr. A. S. Taylor has suggested that a very susceptible paper for detect-
ing alkalies may be prepared by steeping it in an acid infusion of rose petals.

produces is highly characteristic, and is particularly perceptible in many *colored* liquids ; we, therefore, cannot well dispense with turmeric paper. When testing with turmeric paper, it is to be borne in mind that, besides the substances enumerated at β., several other bodies (boracic acid, for instance,) possess the property of turning its yellow color to brown. All reagent papers are to be cut into slips, and kept in small, well-closed boxes, or stoppered phials,

§ 25.

2. SULPHURIC ACID. (SO₃).

H_2SO_4

Sulphuric acid of commerce, freed from nitric acid by boiling is sufficiently pure for the purposes of qualitative analysis.* Should it, however, contain arsenic, this must be removed before the acid can be applied for the detection of arsenic by Marsh's method. The following process will serve to effect this purpose. The acid is to be diluted with six time its amount of water, and the fluid saturated with sulphuretted hydrogen ; the mixture is then allowed to stand in a moderately warm place until it is perfectly clear, when the fluid is to be filtered off from the precipitated sulphuret of arsenic. The filtrate is finally boiled until it is perfectly inodorous.

Test.—Sulphuric acid, when boiled with a small portion of indigo solution, must not destroy its blue color. When mixed with pure zinc and water, it must yield hydrogen, which, on being passed through a red-hot tube, does not deposit the slightest trace of arsenic. (Compare § 95, *d.*)

Uses.—Sulphuric acid has to most bases a greater affinity than almost any other acid ; it is therefore used principally for the liberation and expulsion of other acids, especially of phosphoric, boracic, hydrochloric, nitric, and acetic acid. It serves also for the liberation of iodine from the iodides. In this process, it oxidizes the metals at the expense of its own oxygen, and is accordingly reduced to the state of sulphurous acid. Several

* The sulphuric acid of commerce often contains lead, which renders it turbid when diluted ; this may be removed by allowing the lead to subside, or by distillation.

D

substances which cannot exist in an anhydrous state (e. g. oxalic acid) are decomposed when brought into contact with concentrated sulphuric acid; this decomposition is owing to the great affinity which sulphuric acid possesses for water. The nature of the decomposed body may in such cases be determined by the liberated products of its decomposition. Sulphuric acid is, moreover, frequently used for the evolution of certain gases, more particularly of hydrogen and sulphuretted hydrogen. Sulphuric acid serves also as a *special* reagent for the detection of baryta, strontia, and lead; the acid intended for this purpose is to be diluted with four parts of water.

§ 26. H_2S

3. SULPHURETTED HYDROGEN.   (H S).
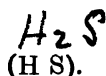
Preparation.—An intimate mixture of thirty parts of iron filings with twenty-one parts of sublimed sulphur is gradually projected in small portions into a red-hot crucible, with this precaution, that the operator awaits always the incandescence of the last introduced portion, before proceeding to the addition of a fresh one. When the whole mixture has thus been introduced into the crucible, the latter is carefully covered, and allowed to continue a short time longer exposed to the fire.

Should the operator possess a blast furnace or a well-draughted wind furnace, he may procure a purer and superior kind of sulphuret of iron, by heating iron borings to the most intense redness in a hessian crucible, and projecting small lumps of sulphur upon the ignited mass, until the whole is converted into sulphuret of iron. A perforation in the bottom of the crucible will be found of some use in this process, as this will allow the sulphuret of iron to run off immediately upon its formation, when it may very conveniently be received in a coal shovel placed in the ash-pit.

The sulphuret of iron produced by either method is broken into lumps, and the latter are introduced into an evolution flask. (Vide Plate III. *a*.)

FIG. 3.
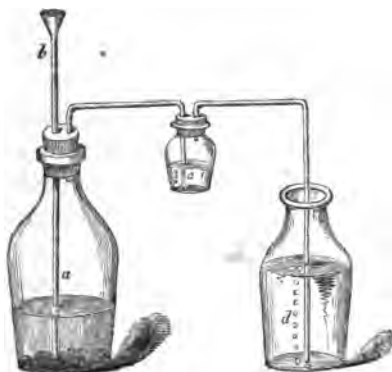
Water is then poured into the flask, and concentrated sulphuric acid added through the funnel-tube b. The evolved gas is purified by transmitting it through some water contained in a small flask (c).

Sulphuretted hydrogen water (solution of sulphuretted hydrogen) is prepared by conducting the purified gas into a flask (d), filled to about three-fourths with cold water and which has been previously freed from air by boiling. This operation is continued until the water is completely saturated with sulphuretted hydrogen gas, which may be readily ascertained by closing the mouth of the flask with the thumb, and strongly agitated its contents : if, upon this, a pressure is felt from within tending to push the thumb off the aperture of the flask, the operation may be considered at an end ; but if, on the contrary, the thumb feels sucked into the mouth of the flask, this is a sure sign that the water is still capable of absorbing more gas.

Sulphuretted hydrogen water must be kept in well-closed vessels, otherwise it will soon suffer complete decomposition. The best way of preserving it unaltered for a very long time is to pour the fresh prepared solution immediately into small phials, and to place the latter, carefully corked, in an inverted position, into small vessels filled with water.

Tests.—Pure sulphuretted hydrogen water ought to be perfectly clear, and should possess the odor of the gas in an eminent degree; when treated with perchloride of iron, it must yield a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it.

Uses.—Sulphuretted hydrogen has a strong tendency to undergo decomposition with metallic oxides forming water and metallic sulphurets; and the latter being mostly insoluble in water, are usually precipitated in the process. The conditions under which the precipitation of certain sulphurets ensues differ materially ;— by altering or modifying these conditions, we may therefore divide the whole of the precipitable metals into groups, as will be found explained at § 27. Sulphuretted hydrogen is therefore an invaluable agent to effect the separation of metals into the principal groups. Some of the precipitated sulphurets exhibit a characteristic color indicative of the individual metals which they respectively contain. Sulphuretted hydrogen serves thus more particularly for the special detection of tin, antimony, arsenic, cadmium, manganese, and zinc. For more ample information upon this point, I refer to the third section. The great facility with which sulphuretted hydrogen is decomposed, renders this substance also a useful reducing agent for many compounds: thus it serves, for instance, to reduce persalt of iron to the state of protosalt, chromic acid to the state of oxide, &c., &c. In such processes of reduction, the sulphur separates in the form of a fine white powder.

§ 27.

4. HYDROSULPHURET OF AMMONIA. $(N\,H_4\,S,\,H\,S)$.

Preparation.—Transmit sulphuretted hydrogen gas through solution of ammonia, to complete saturation, i. e., until the mixture ceases to precipitate a solution of sulphate of magnesia.

The hydrosulphuret of ammonia, thus prepared, must be kept in well-stoppered bottles, since contact with the atmosphere would cause its decomposition.

Tests.—Hydrosulphuret of ammonia is colorless at first, and deposits no sulphur on being mixed with acids; when exposed to the contact of the air, it acquires a yellow tint, owing to the formation of pentasulphuret of ammonium. (NH_4, S_5.) This yellow coloration does not render the reagent unfit for use; but it is to be borne in mind that it will *now* deposit sulphur when mixed with acids. Hydrosulphuret of ammonia must be transparent; upon the application of heat, it must volatilize without leaving a residue; and, as already stated, it ought not to precipitate solution of sulphate of magnesia.

Uses.—I mentioned already in the preceding paragraph that the separation of the metallic oxides precipitable by sulphuretted hydrogen, and their consequent arrangement into groups, depends upon certain conditions respectively necessary for their precipitation. The *presence* of an alkali forms one of these conditions— its *absence* forms another—which means that certain sulphurets precipitate only when the menstruum is alkaline, because they are soluble in acids; whilst others precipitate only when the menstruum is acid, since they are soluble in alkaline sulphurets. Now the hydrosulphuret of ammonia may be looked upon as a reagent in which sulphuretted hydrogen acts in conjunction with ammonia; we have here accordingly the conditions necessary to effect the precipitation of the above mentioned first group of sulphurets, combined with those needful, either to *prevent* the precipitation of the sulphurets of the other group, or to effect their re-solution, when precipitated from acid solutions, —the precipitate being digested with the reagent. Hydrosulphuret of ammonia intended for the latter purpose must, in certain cases, contain an excess of sulphur.

Besides the sulphurets, the precipitation of which is effected by the joint action of sulphuretted hydrogen and of ammonia, hydrosulphuret of ammonia precipitates, by the sole action of its ammonia, alumina and oxide of chromium as hydrated oxides, and also substances contained in a state of simple solution in a free acid; thus it precipitates, for instance, phosphate of lime from its solution in hydrochloric acid;—this property of hydrosulphuret of ammonia must not be lost sight of in experiments.

§ 28.

5. SULPHURET OF POTASSIUM. $(K O, S_2 O_2 + KS_2)$.

Preparation.—This reagent must be prepared fresh every time when needed for use.   The best way of invariably ensuring the production of a sulphuret of potassium of uniform composition, is to divide a certain quantity of solution of potass into two equal portions, to boil the one portion with sulphur in excess, to decant the dark yellow fluid from the undissolved sulphur, and to mix the decanted liquid with the other portion of the potassa solution.

Uses.—Sulphuret of potassium is substituted for hydrosulphuret of ammonia, to effect the separation of sulphuret of copper from such compounds of sulphur as are soluble in alkaline sulphurets, from protosulphuret of tin, for instance, since sulphuret of copper is not quite insoluble in hydrosulphuret of ammonia.

§ 29.

6. POTASS. $(K O)$.

Preparation.—Dissolve one ounce of pure carbonate of potassa (vide § 30) in twelve ounces of water, pour the solution into a clean iron pan, and heat to boiling.   Keep the fluid in constant ebullition, and add hydrated lime in small portions until a sample of the mixture ceases to cause the slightest effervescence when filtered into hydrochloric acid.   (Two parts of carbonate of potassa require the hydrate of about one part of caustic lime.)   The vessel must now be removed from the fire, and if the preceding directions have been carefully followed, the carbonate of lime which is formed will quickly subside to the bottom of the pan; as soon as this takes place, the solution is poured into a bottle closely stopped, and when quite bright draw off the clear solution and evaporate over a rapid fire in an iron pan, or, better still, in a silver basin, until reduced to four ounces, which will accordingly give a specific of gravity of 1·33.

Solution of potassa is most safely kept in a small flask, closed by means of ground glass caps instead of stoppers; in default of capped flasks, common bottles with ground stoppers may be used, with this precaution, that a small slip of writing paper be rolled round

the stopper, otherwise it will, after the lapse of a short time, be found impossible to take the stopper off

Tests.—Solution of potassa must be colorless. After supersaturation with nitric acid, (which process should be attended with slight effervescence only,) it must yield no precipitate, neither with solution of chloride of barium nor with solution of nitrate of silver; nor ought the residue which remains upon evaporation to dryness leave any silicic acid when redissolved in water. Finally, solution of potassa lay ought not to be rendered turbid when heated with an equal measure of solution of sal ammoniac.

Uses.—The great affinity which potassa possesses for acids renders this substance a powerful agent to effect the decomposition of the salts of most bases, and consequently the precipitation of those bases which are insoluble in water. Many of the thus precipitated oxides redissolve in an excess of potassa; such are, for instance, alumina, oxide of chromium, oxide of lead; whilst others remain undissolved, e. g. peroxide of iron, oxide of bismuth, &c., &c. Potassa serves therefore also as a means to separate the former from the latter. Potass possesses, moreover, a solvent power for many salts, (e. g. chromate of lead,) sulphurets, &c., &c., and enables us thus to separate and distinguish them from other substances. Many of the oxides precipitated by the action of potassa exhibit a peculiar color or possess other characteristic properties which may serve to lead to the detection of the individual metal which they respectively contain; such are, for instance, the precipitates of protoxide of manganese, protoxide of iron, proxide of mercury, &c., &c. Potass expels ammonia from its salts, and enables us thus to detect the latter substance by its odor, its reaction on vegetable colors, &c., &c.

§ 30. K_2CO_3

7. CARBONATE OF POTASSA. (KO,CO_2).

Preparation.=Ignite purified and thoroughly-washed bitartrate of potassa in an iron pan, to complete carbonization, boil the residue with water, filter the solution, and evaporate it to dryness in a clean iron pan, taking care towards the conclusion of the process to keep stirring the mass without interruption; keep

the.dry salt in a well-closed bottle. When required for use, dissolve one part of the dry salt in five parts of water.

Tests.—Carbonate of potassa intended for analytical purposes must be perfectly white. Neither chloride of barium nor nitrate of silver must render its solution turbid, after supersaturation with nitric acid; nor ought the residue which remains upon evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, leave any silica when redissolved in water.

Uses.—With the exception of the alkalies, carbonate of potassa precipitates the whole of the bases, most of them as carbonates, but some also as oxides. Those bases which are soluble in water as bicarbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of carbonate of potassa exhibit a characteristic color which may lead to the detection of the individual metals which they respectively contain. Solution of carbonate of potassa serves moreover for the decomposition of many insoluble salts of the alkaline earths, or with metallic bases, and more particularly of those with organic acids; upon boiling such salts with carbonate of potassa, double decomposition ensues, the base of the salt combining with the carbonic acid, whilst the liberated acid combines with the potassa, and is thus obtained in solution in the form of a potassa salt. Carbonate of potassa is used also to saturate free acids, and thus to obtain them in the form of potassa salts. This substance finally is used as *a special* reagent, in which capacity it serves to precipitate platinum from solutions containing hydrochloric acid.

§ 31. NH_3

8. AMMONIA. (NH_4, O).

Preparation.—The apparatus illustrated by Plate III. (vide § 26) may also serve for the preparation of solution of ammonia, with this modification, however, that no funnel tube being required in this process, the cork upon the flask *a* has only one perforation for the reception of the tube which serves to conduct the evolved ammonia into the washing bottle. The

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washing should contain only a very small amount of water, whilst the flask d, which is intended for the final reception of the washed gas, must contain ten parts of water. The operation commences by slaking four parts of caustic lime with $1\frac{1}{3}$ parts of water; the thus produced hydrate is introduced into a, and mixed with five parts of sal ammoniac in powder; water is then cautiously added sufficient to form the powder into lumps when agitated. The flask a is then connected with the rest of the apparatus, and placed in a sand-bath, the flask d standing in a vessel with cold water. The evolution of gas will now speedily ensue, upon the application of heat, which latter is to be continued until no more bubbles appear. The cork is quickly removed from the flask a, to prevent the receding of the fluid. The solution of ammonia contained in the washing bottle is impure, but that contained in the receiver d is perfectly pure; it contains about 16 per cent. of ammonia, and has accordingly a specific gravity of about 0·93. It is to be kept in bottles closed with ground stoppers.

Tests.—Solution of ammonia must be colorless, and ought not to leave the slightest residue when evaporated on a watch-glass, nor should it cause the slightest turbidity in lime-water (carbonic acid). Neither nitrate of baryta, nor nitrate of silver, should render it turbid after supersaturation with nitric acid, nor should sulphuretted hydrogen impart to it the slightest color.

Uses.—Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid fluids, and also to effect the precipitation of a great many metallic oxides and earths; many of these precipitates redissolve in excess of ammonia as ammoniacal double salts, for instance, the oxides of zinc, cadmium, silver, copper, &c., &c., whilst others are insoluble in free ammonia. This reagent may serve, therefore, to separate and distinguish the former from the latter. Some of these precipitates, as well as their ammoniacal solutions, exhibit a peculiar color, which may at once lead to the detection of the individual metals which they respectively contain.

Many of those oxides which are precipitated by ammonia from

neutral solutions, are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the formation of an ammoniacal salt. Compare § 23, chloride of ammonium. *

§ 32. $(NH_4)_2 CO_3$

9. CARBONATE OF AMMONIA. (NH_4, O, CO_2).

Preparation.—We use, for the purposes of chemical analysis, purified sesquicarbonate of ammonia, entirely free from any smell of animal oil, (such as is prepared on a large scale, by the sublimation of sal ammoniac and chalk). The outer and inner surface of the mass are to be carefully scraped. One part of this salt is to be dissolved in a mixture of four parts of water with one part of caustic solution of ammonia.

Tests.—Pure carbonate of ammonia must completely volatilize. Neither solution of nitrate of baryta, nor of nitrate of silver, nor sulphuretted hydrogen, should color or precipitate it, after supersaturation with nitric acid.

Uses.—Carbonate of ammonia precipitates, like carbonate of potassa, most metallic oxides and earths. The complete precipitation of many of them ensues equally only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner, carbonate of ammonia dissolves many hydrated oxides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent. This power of solution rests upon the tendency of the ammoniacal salts to form soluble double salts, which are indecomposable by free ammonia as well as by carbonate of ammonia.

Carbonate of ammonia, like caustic ammonia, and for the same reason, fails to precipitate from acid solutions, many oxides

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* The explanation of many chemical transformations into which the ammoniacal compounds enter, is greatly facilitated by assuming both as regards its oxygen salts and also the aqueous solution of chloride of ammonium, that it exists as oxide of ammonium, $N H_4 O$, instead of ammonia $N H_3$, which has no analogy with other bases. In the present edition, ammonia signifies oxide of ammonium $N H_4 O$, and corresponds to the oxides of potassium and sodium, or potassa and soda.

which it precipitates from neutral solutions. (Compare § 81.) We use carbonate of ammonia, in chemical analysis, principally to effect the precipitation of baryta, strontia, and lime, and the separation of these substances from magnesia, since the latter is not precipitated by this reagent in the presence of ammoniacal salts.

§ 33.

10. CHLORIDE OF BARIUM. (Ba Cl).

Preparation.—Six parts of finely levigated sulphate of baryta are mixed with one part of powdered charcoal and one and a half part of flour ; the mixture is introduced into a hessian crucible, and the latter exposed to the strongest possible red heat. The fused and refrigerated mass is levigated ; about nine-tenths of the powder is then boiled with four times its weight of water, and hydrochloric acid is added, until all effervescence of sulphuretted hydrogen ceases, and the fluid begins to manifest a feebly acid reaction. The last tenth of the powder is then added, and the boiling still continued for some time. The alkaline fluid is subsequently filtered, and the filtrate crystallized. The crystals when dry are digested and thoroughly washed with alcohol, redissolved in water, and the solution finally re-crystallized. For use, one part of the crystals is dissolved in ten parts of water.

Tests.—Pure chloride of barium must not alter vegetable colors, nor ought its solution to be colored or precipitated by sulphuretted hydrogen, nor by hydrosulphuret of ammonia. Pure sulphuric acid must precipitate every fixed particle from it, so that the fluid filtered off from the precipitate formed upon the addition of the test fails to leave the slightest residue when evaporated on a platinum plate.

Uses.—Baryta forms with many acids soluble, and with others, insoluble, compounds. This property of baryta affords us a means of distinguishing the former acids, which are not precipitated by chloride of barium, from the latter in the solution of the salts of which this reagent produces a precipitate. The deportment which the precipitated salts of baryta respectively manifest with other substances (acids) differs. Accordingly, by subjecting the salts

to the action of such substances, we are enabled to subdivide the group of precipitate acids, and even to detect certain individual acids, and more particularly sulphuric acid.   This renders chloride of barium one of our most important reagents.

§ 34.

11. NITRATE OF BARYTA.   (Ba·O, N O$_5$).

Preparation.—A dilute solution of chloride of barium is boiled, and carbonate of ammonia added, as long as a precipitate continues to form, and therefore until the liquid manifests an alkaline reaction.   The carbonate of baryta obtained by this process is carefully washed, and subsequently projected into hot dilute nitric acid, until the fluid ceases to manifest an acid reaction.   The solution is then filtered, and the filtrate subsequently evaporated to crystallization.   For use, one part of the crystallized salt is dissolved in ten parts of water.

Tests.—The purity of nitrate of baryta is tested by the same means as that of chloride of barium (§ 33).   Nitrate of silver must not render its solution turbid.

Uses.—Nitrate of baryta is analogous in its action to chloride of barium, and may be substituted for this latter substance in cases where it is desirable to avoid the presence of a metallic chloride.

§ 35.

12. CHLORIDE OF CALCIUM.   (Ca Cl).

Preparation.—Chalk is added to hot dilute hydrochloric acid, until all acid reaction ceases; the solution is then filtered, and some ammonia added to it; the mixture is allowed to stand a few hours, at a moderate heat, and is afterwards filtered; the filtrate is subsequently heated to boiling, and carbonate of ammonia added until the lime is completely precipitated; the precipitated carbonate of lime is to be thoroughly washed.   A mixture of one part of pure hydrochloric acid with five parts of water is now heated and the washed carbonate of lime addded to complete neutralization; the solution is boiled up several times, and subsequently filtered, and kept for use.

Tests.—Solution of chloride of calcium must be perfectly neutral, and neither be colored nor precipitated by hydrosulphuret of ammonia; nor ought it to evolve ammonia when mixed with potassa or with hydrate of lime.

Uses.—Chloride of calcium is, in its action and application, analogous to chloride of barium. For, as the latter reagent is used to divide the *inorganic* acids into groups, so chloride of calcium serves in the same manner to effect the separation of the *organic* acids into groups, since it precipitates some of them, whilst it forms soluble compounds with others. And, as is the case with the baryta precipitates, the different conditions under which the various insoluble lime salts are precipitated, enable us to subdivide the group of precipitable acids, and even to detect certain individual acids.

§ 36.

13. NITRATE OF SILVER. (AgO, NO_3).

Preparation.—To obtain nitrate of silver in a state of purity, silver alloyed with copper, a piece of standard coin for instance, is dissolved in nitric acid. The solution is evaporated to dryness, and the residue fused in a small porcelain basin over a spirit-lamp, at a moderate heat, until the nitrate of copper is completely decomposed, that is, until the salt has completely lost its green color, even in the portions adhering to the upper sides of the basin, and the aqueous solution of a sample of it fails to turn blue upon addition of ammonia in excess. The mass is then allowed to cool and subsequently boiled with water; the solution of nitrate of silver is filtered off from the insoluble oxide of copper, and the filtrate finally made to crystallize. One part of the crystals is dissolved in twenty parts of water, for use. The oxide of copper which remains upon the solution of the fused mass, contains invariably a slight admixture of silver. To recover this, the residuary oxide of copper is redissolved in nitric acid, and the silver subsequently precipitated from the solution in the form of chloride of silver.

Tests.—Solution of nitrate of silver must be completely precipitated by dilute hydrochloric acid, so that the fluid filtered off

from the precipitated chloride of silver, leaves no residue w
evaporated on a watch-glass, and is, moreover, neither precipit
nor colored by sulphuretted hydrogen.

Uses.—Oxide of silver forms with many acids soluble, v
others insoluble compounds. Nitrate of silver may, therefo
serve, like chloride of barium, to effect the separation and arrange-
ment of acids into groups.

Most of the insoluble compounds of silver dissolve in dilute
sulphuric acid; chloride, bromide, iodide and cyanide of silver
are insoluble in that menstruum. Nitrate of silver is therefore
a most excellent agent to distinguish and separate from all other
acids, the hydracids corresponding to the last-enumerated four
compounds of silver. Many of the precipitated salts of silver
exhibit a peculiar color, (chromate of silver, arseniate of silver,)
or manifest a characteristic deportment with other reagents, or
upon the application of heat; (formiate of silver;) nitrate of
silver is consequently a very important agent for the direct detec-
tion of certain individual acids.

§ 37.

14. PERCHLORIDE OF IRON. $(Fe_2 Cl_3)$.

Preparation—Heat a mixture of two parts of hydrochloric
acid, and from six to eight parts of water, with an excess of small
iron nails free from rust, until the evolution of hydrogen ceases;
decant the solution into a very capacious vessel, and add one
part of hydrochloric acid to the decanted fluid. Heat the mix-
ture to boiling, and drop nitric acid cautiously and gradually into
the boiling fluid until the addition of this reagent ceases to
produce effervescence of nitric oxide gas, and evolution of
nitrous acid fumes, and until a sample of the fluid fails to
impart a blue color to a solution of ferricyanide of potassium,
(§ 44). A small excess of nitric acid, however, does no harm.
Dilute the solution with water, heat to boiling, add ammonia to
alkaline reaction, and wash the produced precipitate of hydrated
peroxide of iron thoroughly with hot water. Now heat a mixture
of two and a half parts of hydrochloric acid with ten parts of
water, and project the still moist precipitate gradually into it until

the last added particles remain undissolved, even upon continued application of heat. Filter the solution finally, and keep the filtrate for use.

Tests.—Solution of perchloride of iron must not contain an excess of acid; this may be readily ascertained by stirring a sample of it with a glass rod, which has previously been dipped in ammonia, when the absence of any excess of acid will be proved by the formation of a precipitate, which shaking of the vessel and agitation of the fluid fail to redissolve. Ferricyanide of potassium must not impart a blue color to it.

Uses.—Perchloride of iron serves to subdivide the group of organic acids which chloride of calcium fails to precipitate, since benzoate and succinate of iron are insoluble, whilst acetate and formiate of iron are soluble. The aqueous solutions of the neutral peracetate and performiate of iron exhibit an intensely red color; perchloride of iron is therefore a useful agent for detecting acetic acid and formic acid. Perchloride of iron is exceedingly well adapted to effect the decomposition of phosphates of the alkaline earths, (vide § 99, *a.* 8.) Finally, this reagent is applied, for the detection of hydroferrocyanic acid, since it produces Prussian blue with this acid.

II. SPECIAL REAGENTS IN THE HUMID WAY.

a. Reagents which serve principally for the detection or separation of individual bases.

§ 38.

1. SULPHATE OF POTASSA. (KO, SO_3).

Preparation—The sulphate of potassa of commerce is purified by re-crystallization, and one part of the pure salt is dissolved in twelve parts of water for use.

Uses.—Sulphate of potassa precipitates from solutions of salts of barytes and strontia the insoluble sulphates of the oxides. It serves, therefore, to effect the detection and separation of baryta and strontia. It produces likewise a precipitate in very highly concentrated solutions of lime, but, in most cases, this precipitate forms only after the lapse of some time; it fails to precipitate di-

'lute solutions of lime. The action of sulphate of potassa is analogous to that of dilute sulphuric acid ; the former reagent is, however, in many cases preferable to the latter, since it does not disturb the neutrality of the solution.

§ 39.

2. PHOSPHATE OF SODA. $(PO_5, 2 Na O, HO)$.

Preparation.—Heat dilute phosphoric acid of commerce, and add solution of carbonate of soda until all effervescence ceases, and the fluid begins to manifest an alkaline reaction.. Filter the fluid and crystallize the filtrate subsequently by evaporation ; purify the produced salt by repeated recrystallization, and dissolve one part of the pure salt in 10 parts of water for use.

Tests.—Solution of phosphate of soda must not become turbid when heated with ammonia. The precipitates which solution of nitrate of baryta and solution of nitrate of silver produce in it, must completely redissolve upon addition of dilute nitric acid.

Uses.—Phosphate of soda precipitates the alkaline earths, and all metallic oxides, by double affinity. It serves in the course of analysis, after the separation of the heavy metallic oxides, as a test for alkaline earths in general; and, after the separation of baryta, strontia, and lime, as a special test for the detection of magnesia, for which latter purpose it is used in conjunction with ammonia, the magnesia precipitating under these circumstances, as basic phosphate of magnesia and ammonia.

§ 40.

3. ANTIMONIATE OF POTASSA. $(KO, Sb O_4)$.

Preparation.—Mix four parts of metallic antimony of commerce with nine parts of nitrate of potassa ; project the mixture gradually into a red-hot hessian crucible, and continue for some time to maintain the latter in a state of ignition. Boil the fused mass subsequently with water until the soluble part is completely extracted; dry the residue, mix 50 parts of it with 24 parts of dry carbonate of potassa, introduce the mixture into a hessian crucible, and expose the latter for 30 minutes to red heat ; keep the thus produced friable mass in a stoppered bottle.—For use, digest one part of the triturated mass with 20 parts of water at a gentle heat.

allow the solution to cool, and filter it when quite cold. The solution obtained upon boiling the *antimonium diaphoreticum non ablutum, (Phar. Bor.)* may likewise be used, since the salts which this solution contains in admixture scarcely impair the susceptibility of the reaction.

Uses.—Antimonic acid forms with soda a salt of extremely difficult solubility. Antimoniate of potassa affords us therefore a means of detecting the presence of soda. Antimonic acid forms, however, insoluble compounds with the alkaline earths, and with most of the metallic oxides. Antimoniate of potassa can, therefore, only serve for the detection of soda in cases where the fluid to be analysed contains simply soda or potassa. For further particulars on this point, I refer to § 86.

§ 41.

4. NEUTRAL CHROMATE OF POTASSA. ($KO, Cr O_3$).

Preparation —Dissolve the bichromate of potassa of commerce in water and add carbonate of potassa to feebly alkaline reaction. Crystallize the yellow fluid thus produced ; wash the crystals thoroughly, and dissolve one part of the salt in ten parts of water, for use.

Uses.—Chromate of potassa decomposes most soluble salts of metallic oxides, by double affinity. Most of the precipitated chromates are very difficultly soluble, and many of them exhibit characteristic colours which lead readily to the detection of the particular metal which they respectively contain. We use chromate of potassa principally as a test for lead, and in the separation of baryta from strontia.

§ 42.

5. CYANIDE OF POTASSIUM. (K Cy).

Preparation.—A portion of ferrocyanide of potassium of commerce is rendered anhydrous by the application of a gentle heat assisted by stirring ; the anhydrous mass is powdered, and eight parts are intimately mixed with three parts of perfectly dry carbonate of potassa. The mixture is to be fused in a covered hessian, or what is still better, in an iron cru-

E

cible, and kept at a low red heat until it becomes clear, and a small portion withdrawn on the end of an iron rod appears quite white on cooling. The crucible must now be removed from the fire and gently tapped, in order to facilitate the deposition of the small particles of iron. The fused cyanide of potassium is then poured into a heated porcelain or silver basin, or upon a clean iron plate; this part of the process must be executed with great care and caution to prevent the passing over of any of the minute particles of iron which have separated in the process of fusion, and subsided to the bottom of the crucible. The cyanide of potassium thus obtained is exceedingly well adapted for analytical purposes, although it contains an admixture of cyanate of potassa which, upon solution in water, is transformed into carbonate of ammonia, and carbonate of potassa, $(KO, NC_2 O + 4 HO = KO, CO_2 + NH_4 O, CO_2)$. The *real* formula for this cyanide of potassium is therefore $= 5 K Cy + KO, Cy O$.—For use, one part of it is dissolved in four parts of distilled water, without application of heat.

Tests.—Cyanide of potassium must be of a milk white color, and perfectly free from any admixture of particles of iron. The solution in water should be perfectly clear. It ought to contain neither silicic acid, nor sulphuret of potassium; the precipitate which salts of lead produce in its solution, must exhibit a pure white appearance, and the residue which its solution leaves upon evaporation after previous supersaturation with hydrochloric acid must yield a perfectly clear solution when treated with water.

Uses.—Cyanide of potassium (containing an admixture of cyanate of potassa) produces in the solutions of most of the salts with metallic oxides, precipitates of metallic cyanides, oxides or carbonates, which are insoluble in water. The precipitated cyanides are soluble in cyanide of potassium, and may therefore be separated from the oxides or carbonates, by further addition of this reagent. Some of the metallic cyanides redissolve invariably in conjunction with the cyanide of potassium as double cyanides, even in presence of free hydrocyanic acid; whilst the metals of others combine with cyanogen, giving rise to the forma-

tion of new radicals, which are thus obtained in solution in combination with potassium. The most common compounds of the latter description are cobaltocyanide of potassium, and ferro and ferricyanide of potassium. These differ from the double cyanides of the former description, particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Cyanide of potassium may consequently serve to separate the metals which form compounds of the latter description from others, the cyanides of which are precipitated by acids from their solution in cyanide of potassium. In the course of analysis, this reagent serves to effect the separation of cobalt from nickel, and also of copper from cadmium. (Compare § 89 and § 92.).

§ 43.

6. FERROCYANIDE OF POTASSIUM. (C_6 N_3 Fe, 2 K=Cfy, 2 K).

Preparation.—Ferrocyanide of potassium is found in commerce sufficiently pure for the purposes of chemical analysis. One part of the salt is dissolved in twelve parts of water, for use.

Uses.—Ferrocyanogen forms with most metals, compounds insoluble in water, and which frequently exhibit highly characteristic colors. These ferrocyanides are formed when ferrocyanide of potassium is brought into contact with soluble salts of metallic oxides, with chlorides, &c., the potassium changing place with the metals. Ferrocyanide of copper and perferrocyanide of iron exhibit the most characteristic colors of all, and ferrocyanide of potassium serves, therefore, particularly as a test for copper and peroxide of iron.

§ 44.

7. FERRICYANIDE OF POTASSIUM.

(C_{12} N_6 Fe$_2$, 3 K= 2 Cfy, 3 K).
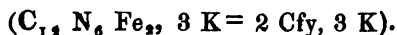
Preparation.—Chlorine gas is to be slowly passed into a solution of one part of ferrocyanide of potassium in 15 parts of water, until the solution shows a fine red color by transmitted light, (a candle answers best,) and tested with perchloride of iron gives neither a blue precipitate nor color. It is then evaporated to dryness in a water-bath, the residue dissolved in four parts of

water, the solution filtered, evaporated quickly to half its bulk, and allowed to crystallize, these crystals are again dissolved in three parts of water, and the solution rapidly evaporated to half, and allowed to crystallize a second time.   One part of the salt is dissolved in ten parts of water, for use.   The solution, as already remarked, must neither produce a blue precipitate nor a blue color, when added to a solution of perchloride of iron.

Uses.—Ferricyanide of potassium decomposes with solutions of metallic oxides, in the same manner as ferrocyanide of potassium. Of the metallic ferricyanides, that of iron is more particularly characterized by its color, and we apply ferricyanide of potassium, therefore, principally as a test for protoxide of iron. Ferricyanide of potassium intended for this purpose may very well be prepared extempore, by gradually adding nitric acid to a solution of ferrocyanide of potassium, until a sample of the mixture ceases to impart a blue color to solution of perchloride of iron.   All elevation of temperature must be avoided in this process, and the vessel ought to be agitated whilst the nitric acid is added.

§ 45.

8. SULPHOCYANIDE OF POTASSIUM. $(Cy\, S_2,\, K)$.

Preparation.—Mix intimately forty-six parts of anhydrous ferrocyanide of potassium, seventeen parts of carbonate of potassa, and thirty-two parts of sulphur; introduce the mixture into an iron pan provided with a lid, and heat to a gentle fusion ; maintain the same moderate heat until the swelling of the mass which ensues at first, has completely subsided and given place to a state of tranquil and clear fusion ; increase the temperature now, towards the end of the operation, to faint redness, in order to decompose the hyposulphite of potassa which has been formed in this process.   Remove the half refrigerated and still soft mass from the pan, break or crush it, and boil the pieces with alcohol. From the thus produced alcoholic solution, part of the sulphocyanide of potassium will separate in colorless crystals, upon cooling; the rest may be obtained by distilling the alcohol off from the mother liquor.   One part of the salt is dissolved in ten parts of water, for use.

Uses.—Sulphocyanide of potassium serves for the detection of peroxide of iron, the presence of which it indicates with the greatest possible precision ; it is in this respect preferable to all other reagents.

§ 46.

9. HYDROFLUOSILICIC ACID.   (Si Fl$_2$, Fl H).

Preparation.—A mixture of one part of sand and one part of fluor-spar in powder is introduced into a glass flask, and six parts of sulphuric acid poured over it; the aperture of the flask is closed with a perforated cork, into which the one end of a bent tube is fitted air-tight.   The other limb of the tube is made to pass to the bottom of a tall flat-bottomed glass jar, into which a small amount of mercury is poured sufficient to cover the extremity of the tube to the extent of several lines ; the mercury is then covered with four parts of water.   The disengagement of fluosilicic gas, which commences even in the cold, is promoted by exposing the flask to a gentle heat, in the sand-bath.   Every gas bubble ascending through the mercury produces in the water a precipitate of hydrated silicic acid.   The rationale of this process is, that of every three equivalents of fluoride of silicon, (Si Fl$_2$), one equivalent decomposes with two equivalents of water into silicic acid (Si O$_2$), which separates, and hydrofluoric acid which combines with the two undecomposed equivalents of fluoride of silicon to hydrofluosilicic acid.

$$[3 \text{ Si Fl}_2 + 2 \text{ HO} = 2 \text{ (Si Fl}_2, \text{ Fl H)} + \text{Si O}_2].$$
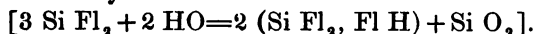
The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the exit tube must be placed under mercury, since it would speedily be choked if this precaution were neglected.   It sometimes happens in the course, and especially towards the end, of the operation, that the gas forms complete tubes or channels of silica in the gelatinous liquid, through which it gains the surface without undergoing decomposition, if they are not occasionally broken by stirring the liquid.   When the evolution of gas has completely ceased, the gelatinous paste is thrown upon a piece of linen, and the fluid squeezed through and subsequently passed through a filter.   The filtrate is kept for use.

Tests.—Hydrofluosilicic acid, mixed with two parts of water, must produce no precipitate in solutions of salts of strontia.

Uses.—Bases decompose with hydrofluosilicic acid, into water, and metallic silicofluorides. Many of the latter are soluble, whilst others are insoluble ; the latter may, therefore, by means of this reagent, be distinguished from the former. In the course of analysis, hydrofluosilicic acid is applied simply for the detection of baryta.

§ 47.

10. OXALATE OF AMMONIA. $(N\ H_4\ O,\ \bar{O})$.

Preparation.—Dissolve commercial oxalic acid in water, add ammonia until the fluid begins to manifest a feebly alkaline reaction, and crystallize. Dissolve one part of the salt previously well washed and dried, in 24 parts of water, for use. Should the salt leave a residue when heated on platinum foil, it must be again crystallized.

Uses.—Oxalic acid forms with many bases salts insoluble in water, consequently oxalate of ammonia causes a precipitate in many metallic solutions, and also in those of lime, baryta and strontia. In analysis it is invaluable for the detection and separation of lime.

§ 48.

11. TARTARIC ACID. $(C_4\ H_2\ O_5 = \bar{T})$.

Tartaric acid is found in commerce sufficiently pure for the purpose of chemical analysis. It is best preserved in powder, since its solution, after some time, suffers decomposition, a white film forming upon its surface.

Uses.—The addition of tartaric acid to a solution of iron, manganese, chromium, alumina, cobalt, and various other metals, prevents the usual precipitation of these metals upon the subsequent addition of an alkali : their non-precipitation is owing to the formation of double tartrates, which are not decomposed by alkalies.

Tartaric acid may serve therefore to effect the separation of these metals, from those the precipitation of which it fails to pre-

vent.   Tartaric acid forms a difficultly soluble acid salt with potassa, but not so with soda ; it is therefore one of our best reagents to distinguish these alkalies from each other.

§ 49.

12. CAUSTIC BARYTA.   (Ba O).

Preparation.—Boil one part of sulphuret of barium (§ 38) with 20 parts of water ; add to the hot solution an excess of pulverized copper scales, and apply heat until a filtered sample of the fluid fails to impart a black color to a solution of acetate of lead. Filter the fluid whilst hot, into a well-closed vessel, allowing it to remain some days in a cool place to crystallize.   After well washing, the crystals are to be digested in water in a closed vessel, the saturated solution must be quickly filtered and kept in a well-stoppered bottle ; should it contain an admixture of copper, this may be readily removed by cautiously adding sulphuretted hydrogen, and filtering the fluid off from the precipitated sulphuret of copper.

Uses.—Caustic baryta is a strong base, and acts similar to lime, i. e, it precipitates the alkaline earths and metallic oxides which are insoluble in water, from the solution of their salts. We use baryta in the course of analysis, simply for the precipitation of magnesia, and for this purpose solution of sulphuret of barium will serve as well, provided it contain an admixture of caustic baryta.*   Water of baryta may serve, moreover, like chloride of barium and nitrate of baryta, to effect the precipitation of those acids which form insoluble compounds with this earth ; in this respect, however, it is principally employed for the detection of carbonic acid.

§ 50.

13. CARBONATE OF BARYTA.   (Ba O, C O_2).

Preparation.—Carbonate of baryta is prepared as explained § 34, in making nitrate of baryta.   The well-washed precipitate

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* Sulphuret of barium contains invariably an admixture of caustic baryta, when not prepared at an *exceedingly* high temperature.

is rubbed up with water, and the milky liquid, which of course must be shaken each time it is used, kept in a stoppered bottle.

Uses.—Carbonate of baryta entirely precipitates peroxide of iron as a hydrate, even from a cold solution, by abstracting its acid ; whilst, under similar circumstances, the protoxides of iron, manganese, oxide of zinc, protoxides of nickel and cobalt, are not precipitated. Thus the carbonate of baryta is an excellent means of separating these latter oxides from the former. It is also useful, as shewn a short time since by Rose in the separation of nickel and cobalt by saturating a solution of the two metals in hydrochloric acid with chlorine, and then adding carbonate of baryta, the cobalt precipitates as a hydrated peroxide, and all the nickel remains in solution.

§ 51.

14. PROTOCHLORIDE OF TIN. (Sn Cl).

Preparation.—Fuse a certain amount of English tin in an iron spoon, and, after having removed the latter from the fire, triturate the fused mass with a pestle until it has completely solidified. Introduce the powder which is thus obtained, into a flask, pour concentrated hydrochloric acid over it, (taking care always, that the tin predominate,) and boil the mixture ; dilute the solution with four times its amount of water, slightly acidulated with hydrochloric acid, and filter. Pour the filtrate into a bottle containing small fragments of metallic tin, and close the mouth carefully. If these precautions be neglected, the protochloride will soon change into perchloride, which, of course, will render the reagent totally unfit for the purpose for which it is intended.

Tests.— Solution of protochloride of tin, when added to a solution of perchloride of mercury, must immediately produce a white precipitate of protochloride of mercury ; when treated with sulphuretted hydrogen, it must yield a dark brown precipitate ; it should not be precipitated, nor rendered turbid by sulphuric acid.

Uses.—The great tendency of protochloride of tin to absorb oxygen, and thus to form peroxide,—or rather perchloride of tin, since the peroxide, in the moment of its formation, decomposes with the free hydrochloric acid present,—renders this substance

one of our most powerful reducing agents. We use this reagent, in the course of analysis, as a test for mercury, and also to effect the detection of gold, for which latter purpose it is previously to be mixed with some nitric acid without heating.

§ 52.

15. PERCHLORIDE OF GOLD. (Au Cl₃).

Preparation.—To produce this reagent, fine shreds of gold, which may be alloyed either with silver or copper, are introduced into a flask, and drenched with an excess of aqua regia; a gentle hert is then applied to the flask, and maintained as long as the metallic mass continues to dissolve. A portion of the solution is then diluted with water, and tested with ferrocyanide of potassium; should this reagent produce a brown red precipitate, this is a sure sign that the gold was alloyed with copper, and the solution is, in that case, to be mixed with solution of protosulphate of iron in excess, when the perchloride of gold will suffer reduction to the metallic state, the gold separating in the form of a fine brownish black powder; the latter is introduced into a small flask, thoroughly washed, and redissolved in aqua regia; the solution is evaporated to dryness in the water-bath, and the residue finally dissolved in thirty parts of water. Should the gold be alloyed with silver, the latter metal will remain as chloride of silver, upon treating the alloy with aqua regia. In this case, the solution is to be at once evaporated to dryness, and the residue dissolved for use in thirty parts of water.

Uses.—Perchloride of gold has a great tendency to yield up its chlorine to other substances, and therefore possesses the property of converting protochlorides into perchlorides, protoxides into peroxides and perchlorides, &c. These peroxidations, &c. are usually indicated by the precipitation of pure metallic gold, in the form of a blackish brown powder. In the systematic course of analysis, this reagent serves exclusively for the detection of protosalts of tin, in the solution of which it produces a purple color, or a purple-colored precipitate. (Vide infra. § 95, b. 6.).

§ 53.

16. BICHLORIDE OF PLATINUM.   (Pt Cl$_2$).

Preparation.—To obtain this reagent, platinum filings, which have been purified previously by boiling with nitric acid, are introduced into a narrow-necked flask, and drenched with concentrated hydrochloric acid; some nitric acid is then added, and a gentle heat applied, with occasional additions of fresh portions of nitric acid; this process is continued until the platinum is completely dissolved. The solution is subsequently evaporated to dryness in the water-bath, some hydrochloric acid being added during the operation; the residue is finally dissolved in ten parts of water.

Uses.—Perchloride of platinum forms very sparingly soluble double salts, with chloride of potassium and chloride of ammonium, whilst the double salt which it forms with chloride of sodium is very readily soluble. It serves, therefore, to detect ammonia and potassa, and is, indeed, our most delicate reagent for the latter substance.

§ 54.

17. ZINC.   (Zn).

Pure sublimed zinc is selected for the purposes of chemical analysis; particular care should be taken to have it perfectly free from arsenic. The method described at § 25 will serve to detect the presence of the slightest trace of this substance. The pure sublimed zinc is to be fused, and a portion of it gradually dropped into a large vessel, containing water; the remainder is to be cast into small cylinders, by pouring the fused metal into wooden moulds, coated with chalk.

Uses.—The great affinity which zinc possesses for oxygen, and its oxides for acids, renders this metal a very valuable agent to effect the reduction of many metallic salts and oxides, and consequent precipitation of the reduced metals. Since the thus precipitated metals vary in colour, form, &c., this reagent may likewise serve for their individual detection. We apply it principally for the precipitation of antimony and of tin. Zinc is moreover frequently used for the evolution of hydrogen.

§ 55.

18. IRON.   (Fe).

Iron, like zinc, reduces many metallic salts and oxides, and precipitates the reduced metals.   We use it especially for the detection of copper, which precipitates upon it with its characteristic color.   Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, &c., will serve for this purpose.

§ 56.

19. COPPER.   (Cu).

We use copper exclusively to effect the reduction of mercurial salts; the metallic mercury precipitates upon the surface of the copper, forming a white coating, which shines with silvery lustre when rubbed.   A copper coin scoured with fine sand, or in fact any clean surface of copper, may be employed for this purpose.

b.   Special reagents, which are principally applied for the detection or separation of individual acids.

§ 57.

1. ACETATE OF POTASSA. $(K O, \overline{A})$.

Preparation.—This reagent is prepared by dissolving one part of pure carbonate of potassa in two parts of water, heating the solution, and saturating it *exactly* with acetic acid.   Acetate of potassa being but rarely employed in analysis, may be prepared as required.

Uses.—Any of the salts of potassa may serve to produce a precipitate of tartar, and therefore to detect tartaric acid; but the acetate of potassa is peculiarly adapted for this purpose, since the precipitated bitartrate of potassa is insoluble in the liberated acetic acid.   Acetate of potassa serves also to precipitate from simple solutions in free mineral acids, certain compounds which are insoluble in acetic acid.   In the systematic course of analysis it is principally applied in the process of the decomposition of the phosphated alkaline earths, to effect the precipitation of the perphosphate of iron from the hydrochloric acid solution.   For the

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latter purpose, however, the acetate of soda, which is more easily purified, may be used with the same results.

§ 58.

2. CAUSTIC LIME.   (Ca O).

Preparation.—Take recently prepared hydrate of lime, and digest it for some time with cold distilled water, with frequent agitation of the mixture; allow the undissolved portion of the lime to subside, decant, and keep the clear fluid in well-stoppered bottles.   Besides lime-water, hydrate of lime should also be kept.

Tests.—Lime-water must impart a deep brown color to turmeric paper, and yield with carbonate of potassa an abundant precipitate. It is totally unfit for use as soon as it loses these properties, which takes place on exposure to air.

Uses.—Lime forms with many acids insoluble, with others soluble salts.   Lime-water may therefore serve to distinguish the former acids from the latter.   Many of these acids are precipitated only under certain circumstances, e. g. on boiling, (citric acid,) and it is therefore easy to distinguish them from one another individually by altering these conditions.   We employ lime-water principally to effect the detection of carbonic acid, and also to distinguish paratartaric acid, tartaric acid, and citric acid, from one another.—Hydrate of lime serves, like caustic potassa, to liberate ammonia, and is in many cases preferable to the latter reagent.

§ 59.

3. SULPHATE OF LIME.   (Ca O, S O$_3$).

Preparation.—To produce this reagent, a concentrated solution of chloride of calcium is mixed with dilute sulphuric acid, the precipitate produced is thoroughly washed, digested, and agitated for some time with water; the undissolved particles are then allowed to subside, and the clear supernatant fluid is decanted and kept for use.

Uses.—Sulphate of lime serves to effect the further subdivision

of those acids which are precipitable by chloride of calcium, since, owing to its difficult solubility, a few acids only of that group (oxalic acid, paratartaric acid,) produce precipitates in its solution. The solution of sulphate of lime serves moreover as a reagent for bases, viz. to distinguish and separate baryta, strontia, and lime from one another, since, of course, it fails to precipitate the latter, whilst it acts upon solutions of baryta and strontia in the same manner as highly dilute sulphuric acid, i. e. it precipitates the baryta immediately, and the strontia only after the lapse of some time.

§ 60.

4. CHLORIDE OF MAGNESIUM.   (Mg Cl).

Preparation.—Chloride of magnesium is prepared by heating a mixture of one part of hydrochloric acid and two and a half parts of water, and adding basic carbonate of magnesia, (magnesiæ carbonas of the shops,) until the liquid ceases to manifest an acid reaction. The solution is once more boiled up, afterwards filtered, and kept for use. Sulphate of magnesia may, in most cases, be substituted for chloride of magnesium.

Uses.—Chloride of magnesium serves almost exclusively for the detection of phosphoric acid, which it precipitates from an aqueous solution of phosphates, in presence of ammonia, in the form of a double salt, (basic phosphate of magnesia and ammonia,) which is nearly insoluble, and possessed of highly characteristic properties. Chloride of magnesium is moreover applid to test the purity of hydrosulphuret of ammonia.   (Vide § 27.)

§ 61.

5. PROTOSULPHATE OF IRON.   (Fe O, S O₃).

Preparation.—To prepare this reagent, iron nails in excess, free from rust, are heated with dilute sulphuric acid until the evolution of hydrogen ceases; the solution is then filtered, and a few drops of dilute sulphuric acid are added to the filtrate, which is then allowed to cool. A sufficiently concentrated solution will yield crystals simply upon cooling; dilute solutions require evaporation for the production of crystals. The crystals

are washed with water slightly acidulated with sulphuric acid, and are then dried and preserved.

Uses.—Protosulphate of iron has a great disposition to absorb oxygen, and to be converted into persulphate of iron. It acts therefore as a powerful reducing agent. We employ it principally for the reduction of nitric acid, which it effects by withdrawing three atoms of oxygen from it, producing nitric oxide. The decomposition of the nitric acid being attended, in this case, with the formation of a very peculiar, intensely brownish black compound of nitric oxide with protosulphate of iron, this reaction is particularly characteristic and sensitive for the detection of nitric acid. Protosulphate of iron serves moreover for the detection of hydro-ferricyanic acid, with which it produces a kind of Prussian blue, and also to effect the precipitation of metallic gold from solutions of the salts of this metal.

§ 62.

6. SOLUTION OF MAGNETIC OXIDE OF IRON (FERROSO-FERRIC OXIDE.)

$$(Fe\ O,\ SO_3 + Fe_2\ Cl_3).$$
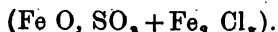
This reagent is not kept on hand, but prepared, when needed, by mixing solution of protosulphate of iron with some perchloride of iron. It serves for the detection of hydrocyanic acid, with which, under certain circumstances, (§ 101. *d.* 4) it yields a precipitate of sesquiferrocyanide of iron. (Prussian blue.)

§ 63.

7. PROTOXIDE OF LEAD.   (Pb O).

Protoxide of lead is employed for the detection of free acetic acid, since it forms with this acid alone, a soluble compound, possessing an alkaline reaction. Finely powdered litharge answers this purpose sufficiently well. (Compare § 105 *a.* 7).

§ 64.

8. NEUTRAL ACETATE OF LEAD.   (Pb O, $\overline{A}$).

The best commercial acetate of lead is sufficiently pure for the

purposes of chemical analysis. One part of the salt is dissolved
in ten parts of water for use.

Uses.—Protoxide of lead forms with a great many acids, com-
pounds which are insoluble in water, and marked either by their
peculiar color or characteristic deportment. The acetate of lead,
for instance, produces precipitates in the solutions of these acids
or of their salts, and contributes essentially to detect and distin-
guish several of them individually. Thus, in particular, chromate
of lead is characterised by its yellow color, phosphate of lead by
its peculiar deportment before the blow-pipe, and malate of lead
by its ready fusibility.

§ 65.

9. BASIC ACETATE OF LEAD. (3 Pb O, $\overline{A}$).

Preparation.—Introduce a mixture of seven parts of finely
powdered litharge with six parts of neutral acetate of lead into a
flask, and pour thirty parts of water over it; close the flask
carefully, and allow it to stand in a moderately warm place, with
occasional agitation of its contents, until the sediment in it is
perfectly white. Decant, and keep the clear fluid in a well-
stoppered bottle. This reagent is unfit for use, if it contains
the slightest admixture of copper; it is necessary, therefore,
to test it with ammonia; should it acquire a blue color upon the
addition of this reagent, this is a sure sign of the presence of
copper, which is to be removed, by digesting the solution with
metallic lead until all the copper is precipitated.

Uses.—The basic acetate of lead, like the neutral acetate, pre-
cipitates those acids which form insoluble compounds with oxide
of lead, and it is more efficient than the latter in those cases
where the compound formed is soluble in acetic acid. We employ it
in analysis especially for the detection of sulphuretted hydrogen,
for which substance it is our most susceptible reagent. It serves,
moreover, to neutralize free acids, in cases where it is desirable to
avoid the application of an alkali, thus it is used, for instance, to
render highly acid solutions of nitrate of bismuth precipitable by
water.

§ 66.

10. HYDRATED OXIDE OF BISMUTH.   (Bi O, H O).

Preparation. — Coarsely-powdered bismuth is gradually projected into pure nitric acid of 1·2 sp. gr. as long as it continues to dissolve in the acid; the operation is to be assisted by the application of a gentle heat.   The solution is diluted with about an equal quantity of warm water, (slightly acidified with nitric acid,) and filtered; the filtrate is mixed with from ten to twenty parts of water, and ammonia added to the milky fluid, until it predominates perceptibly; the mixture is then heated, and the precipitate which has formed in it is then washed, first by decantation, and finally upon a filter; the washed precipitate is afterwards dried between some sheets of blotting-paper, at a moderate heat.

Uses.—The oxide of bismuth, when boiled with alkaline solutions, of metallic sulphurets, decomposes with the latter, giving rise to the formation of metallic oxides, and sulphuret of bismuth.   It is better adapted for this purpose than oxide of copper, since it enables the operator to judge immediately upon the addition of a fresh portion whether the decomposition is complete or not.   It has still another advantage over oxide of copper, since it does not, like the latter, dissolve in the alkaline fluid, presence of organic substances, nor does it act as a reducing agent upon reducible oxygen compounds.   We use the hydrated oxide of bismuth principally to convert sulpharsenious and sulpharsenic acids into arsenious and arsenic acids, for which purpose oxide of copper is altogether inapplicable, since it converts the arsenious acid immediately into arsenic acid, being itself reduced to the state of sub-oxide.

§ 67.

11. SULPHATE OF COPPER.   (Cu O, SO₃).

Preparation.—The sulphate of copper of commerce, purified by recrystallization, is perfectly well adapted for the purposes of chemical analysis.

Uses.—Sulphate of copper is employed in qualitative analysis,

to effect the precipitation of hydriodic acid as protiodide of copper. For this purpose it is necessary to mix the solution of one part of the sulphate of copper with two parts and a quarter of protosulphate of iron, otherwise half of the iodine will separate in a free state. The protoxide of iron is peroxidized in this process at the expense of the oxygen of the oxide of copper, which latter is thus reduced to the state of suboxide. Sulphate of copper is used, moreover, as a test for arsenious and arsenic acids, and in this respect it is a very *delicate*, but by no means a *characteristic* reagent. For this purpose it is best to convert the sulphate into ammonio-sulphate of copper by adding ammonia to its solution until the precipitate which forms at first, is just redissolved. Sulphate of copper with the addition of potassa, is however a most excellent means to distinguish arsenious acid from arsenic acid, since the presence of the former acid is indicated at once by the separation of red oxide (suboxide) of copper. Compare § 95, *d.* 7. Sulphate of copper may also serve to detect the presence of hydroferrocyanic acid.

§ 68.

12. PROTONITRATE OF MERCURY. ($Hg_2 O, NO_5$).

Preparation.—To prepare this reagent, nine parts of nitric acid, of 1.23 sp. gr., are gently heated in a small flask, with ten parts of mercury, until the disengagement of nitrous acid fumes ceases; the solution is then boiled for some time with the undissolved portion of the mercury, taking care to replace the evaporated water, and this process is continued until the whole of the mercury contained in a sample of the fluid is precipitated as protochloride, upon the addition of a solution of common salt in excess, so that protochloride of zinc fails to produce the slightest precipitate in the liquid filtered off from the precipitated protochloride. The solution is then agitated with the undissolved mercury until cold; the crystals obtained are powdered, and agitated with twenty parts of cold water, slightly acidulated with nitric acid. The fluid is then filtered, if necessary, and the filtrate kept in a glass bottle, the bottom of which is covered with mercury.

F

Uses. — The protonitrate of mercury acts in an analogous manner to the corresponding salt of silver. In the first place, it precipitates many acids, especially the hydracids; and secondly, it serves for the detection of several readily oxidizable substances, e. g. of formic acid, since the oxidation of such substances, at the expense of the oxygen of the black oxide of mercury, is attended with the highly characteristic separation of metallic mercury.

§ 69.

13. PEROXIDE OF MERCURY. (Hg O).

The peroxide of mercury of commerce is very finely powdered, previously to which it should be moistened with some alcohol to prevent minute particles rising into the air. The powder is kept for use. Peroxide of mercury is a safe and characteristic reagent for hydrocyanic acid, since it dissolves in alkaline fluids only when this acid is present. (Compare § 101, *d.* 5).

§ 70.

14. PERCHLORIDE OF MERCURY. (Hg Cl).

The commercial perchloride of mercury is sufficiently pure for the purposes of chemical analysis. One part of the salt is dissolved in sixteen parts of water.

Uses.—Perchloride of mercury yields with various acids, e. g. with hydriodic acid, precipitates of characteristic color, but it is, nevertheless, one of the least essential reagents for the determination of individual acids. It serves also as an oxidizing agent, and enables us to detect the presence of readily oxidizable bodies, e. g. of protoxide of tin, by the precipitation of protochloride of mercury, attendant upon their oxidation.

§ 71.

15. SULPHUROUS ACID. (S O₂).

Preparation.—Introduce some small pieces of charcoal into a flask, add from six to eight times their weight of sulphuric acid, apply heat, and conduct the evolved and washed gas into cold

water, taking care to keep the receiver cool; continue the process
until the water ceases to absorb sulphurous acid.   The solution
thus obtained must be kept in well-stoppered bottles.

Uses.—Sulphurous acid has a great tendency to absorb oxygen
and thus to be converted into sulphuric acid.   It is, therefore,
one of our most powerful reducing agents, and effects the preci-
pitation of metallic mercury from solutions of mercurial salts, and
the reduction of chromic acid to oxide of chromium, as proto-
chloride of tin does.   We employ sulphurous acid principally to
convert arsenic acid into arsenious acid, as a preliminary and
greatly facilitating step towards the subsequent precipitation of
the arsenic by means of sulphuretted hydrogen, (vide § 95, *e*. 3.)
Before applying this reagent, it is always necessary to ascertain
by the smell whether it is fit for use.

§ 72.

16. SULPHITE OF SODA.   (Na O, S O$_2$).

Preparation.—A stream of well-washed sulphurous acid gas,
generated as directed, § 71, is passed into a solution of carbonate
of soda until it is saturated.

Uses.—Sulphite of soda can in almost all cases be substituted
for sulphurous acid, and is preferable to the latter in as much as its
aqueous solution contains the sulphurous acid in a more concen-
trated form, and at the same time is not so readily decomposed.
It is used to convert persalts of iron into protosalts, as in
the examination of small quantities of iron stone, ochreous earths,
&c. for phosphoric acid.

§ 73.

17. CHLORINE.   (Cl).

Preparation.—Introduce one part of peroxide of manganese
in powder into a flask, and add from four to five parts of com-
mercial hydrochloric acid; apply a gentle heat, and conduct the
evolved gas into a jar containing from thirty to forty parts of water,
which must be kept as cool as possible.   The chlorine water
must be preserved in a well-closed bottle, and protected from
the influence of light, since if this precaution be neglected,

the reagent will soon become completely decomposed, i. e. converted into dilute hydrochloric acid, with evolution of oxygen, (owing to the decomposition of water).

Uses.—Chlorine has a greater affinity than iodine and bromine for metals and for hydrogen. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. As free chlorine forms with bromine, chloride of bromine, and with iodine, chloride of iodine, and these compounds present a different deportment from that of the free metalloids, the greatest care must be taken, in certain cases, e. g. when testing for iodine by means of starch, (§ 101, *c.* 8), to avoid adding chlorine water in excess. Chlorine serves, moreover, for the destruction of organic substances, by withdrawing hydrogen from the water, which contains these substances, so that the liberated oxygen is enabled to combine with the vegetable matter, and thus to effect their decomposition. For this latter purpose it is most advisable to *evolve* the chlorine in the fluid, which contains the organic substances; this is effected by the addition of hydrochloric acid to the fluid, heating the mixture to boiling, and adding chlorate of potassa. This gives rise to the formation of chloride of potassium and water, and to the disengagement of chloroso-chloric acid, $(2 \ Cl \ O_5, \ Cl \ O_3)$, which acid acts analogous to Chlorine.

§ 74.

18. SOLUTION OF INDIGO.

Preparation.—One part of indigo powder is heated with seven parts of fuming sulphuric acid. For use, the solution obtained is diluted with just so much water that the fluid still appears distinctly blue.

Uses.—Indigo is decomposed upon boiling with nitric acid, and this decomposition is attended with the formation of oxidation-products of a yellow color. Solution of indigo serves therefore for the detection of nitric acid, both in a free state and in nitrates, in which latter, however, the nitric acid must first be liberated by means of sulphuric acid.

§ 75.

19. STARCH-PASTE.

Common starch is rubbed with cold water, and the mixture heated to boiling, with constant stirring   The paste must be uniform, and so thin as almost to run.

Uses.—Starch, when brought into contact with free iodine, forms with the latter substance a peculiar dark-blue compound, the color of which is so intense that it remains distinctly perceptible, even though the two substances be brought together, in a highly dilute state.   Starch-paste is therefore a most excellent and delicate test for free iodine.   It is far less sensitive with regard to bromine, the fiery yellow color of bromide of starch being by no means so characteristic and intense, as the blue of iodide of starch.

B. REAGENTS IN THE DRY WAY.

1. *Fluxes and decomposing agents.*

§ 76.

1. MIXTURE OF CARBONATE OF SODA AND CARBONATE OF POTASSA.

$$(Na \, O, \, C \, O_2 + K \, O, \, C \, O_2).$$
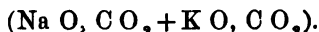
Preparation.—Ten parts of effloresced carbonate of soda are intimately mixed (by trituration) with thirteen parts of dry carbonate of potassa; the mixture is kept in a closed vessel.

Uses.—When silicic acid or silicates are fused with about four parts, (and consequently with an excess,) of carbonate of potassa or soda, carbonic acid escapes with effervescence, and a basic alkaline silicate is formed, which, being soluble in water, may be readily separated from such metallic oxides as it may contain in admixture; from this basic alkaline silicate hydrochloric acid separates the silicic acid invariably in its soluble modification.   It is, however, most commonly used for the detection and separation of silicic acid; the melted mass is treated with hydrochloric (or nitric) acid and water, evaporated to dryness, and the residue warmed with a little hydrochloric or nitric acid; water is

added, and the metallic solution filtered from the now insoluble silica. When a fixed alkaline carbonate is fused with sulphate of baryta, of strontia, or of lime, there is formed an alkaline sulphate with carbonate of baryta, strontia, or lime; in these new compounds, both the acid and base of the prieviously insoluble sulphate, may now be readily detected and determined. We use neither carbonate of potassa alone, nor carbonate of soda alone, to effect the decomposition of the insoluble silicates and sulphates; but we apply for this purpose the above described mixture of both, because this mixture requires a far lower degree'of heat for fusion, than either of its two components, and thus enables us to conduct the operation over a BERZELIUS' lamp. The fusion with alkaline carbonates is invariably effected in a platinum crucible, provided no reducible metallic oxides be present.

§ 77.

2. HYDRATE OF BARYTA. (Ba O, H O).

Preparation.—The crystals of baryta prepared according to the directions given at § 49, are heated gently in a porcelain crucible until the water of crystallization is completely expelled. The residuary white mass is powdered, and kept for use in a well-closed bottle.

Uses.—Hydrate of baryta fuses at a gentle red-heat without losing its water. Upon fusing silicates with about four parts of hydrate of baryta, a superbasic silicate of baryta is formed, and the oxides are liberated. Now, upon treating the fused mass with hydrochloric acid, evaporating the solution to dryness, and digesting the residue with hydrochloric acid, the silicic acid is separated, and the oxides are obtained in solution in the form of chlorides. We use hydrate of baryta as a flux when we wish to test silicates for alkalies. This reagent is preferable as a flux to the carbonate or nitrate of baryta, since it does not require a very high temperature for its fusion, as is the case with the carbonate of baryta, nor does it cause any spirting in the fusing mass, arising from disengagement of gas, as is the case with the

nitrate of baryta. Fluxing with hydrate of baryta is effected in silver or platinum crucibles.

§ 78.

3. NITRATE OF POTASSA. $(K O, N O_5)$.

Preparation.—Dissolve commercial nitre in boiling water to complete saturation; dilute the solution with a small portion of water, filter hot into a beaker-glass, place the latter in water, and stir the solution till cold. Transfer the crystalline powder thus obtained, to a filter, and wash it with cold water until the washings cease to be rendered turbid by nitrate of silver. Dry it, and keep for use.

Tests.—A solution of nitrate of potassa must neither be rendered turbid by solution of nitrate of silver, nor nitrate of baryta, and it ought not to be precipitated by carbonate of potassa.

Uses.—Nitrate of potassa serves as a very powerful oxidizing agent, by yielding oxygen to combustible substances when heated with the latter. We use this reagent principally to convert several metallic sulphurets, and more particularly the sulphurets of tin, antimony, and arsenic, into oxides and acids. In the detection of antimony when arsenic is present, and to separate the two, nitrate of soda (formed by saturating pure carbonate of soda with nitric acid) is to be preferred to nitrate of potassa. We use nitrate of potassa also to effect the rapid and complete combustion of organic substances; for the latter purpose, however, nitrate of ammonia is in many cases preferable; this reagent is prepared by saturating nitric acid with carbonate of ammonia.

II. BLOW-PIPE REAGENTS.

§ 79.

1 CHARCOAL.   (C).

Any kind of thoroughly calcined wood-charcoal may be used for blow-pipe experiments. The charcoal of pine or linden-wood is however preferable to any other sort. Smooth pieces ought to

be selected, as when knotty they split on heating, and thus throw off portions of the matter under examination.

Uses.—Charcoal is chiefly employed, in blow-pipe experiments, as a support for the substance under examination, (vide § 13). The following are the properties which render it so valuable in this respect.   1st, its infusibility; 2nd, its low conducting power for heat, which admits of substances being heated more strongly upon a charcoal than upon any other support; 3rd, its porosity, by means of which it imbibes readily fusible substances, such as borax, carbonate of soda, &c., whilst infusible bodies remain on its surface; 4th, its property of reducing oxidized bodies, by which it greatly assists the reduction of oxides by the inner flame of the blow-pipe.—Charcoal serves, moreover, to effect the reduction of arsenious acid and of arsenic acid, since, at a red-heat, it withdraws the oxygen from these acids.   For this purpose, the charcoal is used either in the form of small splinters, or as a coarse powder.   The separation of the arsenic from its acids requires sometimes the united application of charcoal and an alkaline carbonate; in such cases it is best to use a mixture of effloresced carbonate of soda and lamp-black; this mixture is to be ignited in a covered crucible, and kept in a well-stoppered bottle.

§ 80.

2. CARBONATE OF SODA. (NaO, CO_2).

Preparation.—An intimate mixture of one part of crystallized and three parts of effloresced carbonate of soda is introduced into the neck of a broken retort, a wide glass tube, or some other vessel of that description; the one aperture of the tube &c. is left open, the other is closed with a perforated cork into which a tube is fitted; this is connected with a gas evolution flask containing carbonate of lime, from which carbonic acid is evolved by means of hydrochloric acid as soon as the whole apparatus is fully prepared.   The evolved carbonic acid combines with the carbonate of soda, and forms bicarbonate. The complete saturation of the carbonate of soda with carbonic acid, is indicated by the fall of the temperature of the

mixture which had become elevated in the course of the process, and by the immediate extinction of an ignited wood-splint, when held before the open aperture of the tube. The salt is now placed upon a filter, and washed with cold water, until the washings cease to be rendered turbid by chloride of barium or nitrate of silver, after previous supersaturation with nitric acid; the salt is then dried, and ignited in a silver, platinum, or porcelain crucible. The ignition of the bicarbonate causes the expulsion of one atom of carbonic acid, and there remains, consequently, simple carbonate of soda. The purity of carbonate of soda is tested by the same means as that of carbonate of potassa. Hydrosulphuret of ammonia must not alter its solution.

Uses.—Carbonate of soda is readily fusible, and is, therefore, peculiarly adapted to promote the reduction of oxidized substances by the inner flame of the blow-pipe. While it enters into fusion, it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. But it does not co-operate in this process by its chemical properties. If the quantity operated upon be very minute, the reduced metal will often be found in the pores of the charcoal. In such cases, the parts surrounding the little cavity which contained the sample are dug out with a knife, triturated in a small mortar, and the charcoal washed off from the metallic particles, which then become visible, either in form of powder or as small and flat spangles, according to the nature of the particular metal or metals present.

In many cases, e g. in the reduction of peroxide of tin, some borax may be advantageously added to the carbonate of soda, in order to render the mass more readily fusible. Carbonate of soda serves also as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in fusing carbonate of soda. The sample to be examined is made into a paste with some carbonate of soda and water; and this paste is placed upon the loop of a platinum wire, and heated. A few only of the bases dissolve in melting carbonate of soda, but acids dis-

solve with facility. Silicic acid differs from all other acids, in as much as the glass which it forms with carbonate of soda remains clear upon cooling, provided, of course, the two constituents be present in the requisite proportions. Carbonate of soda is moreover applied as a decomposing agent and flux, and more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, whilst, at the same time, the new-formed sulphate of soda is reduced to sulphuret of sodium,—and of the sulphurets of arsenic with which it forms sulphuret of arsenic and sodium, and arsenite or arseniate of soda, thus converting the arsenic into a state which permits its subsequent reduction by hydrogen. Finally, carbonate of soda is the most sensitive reagent in the dry way, for the detection of manganese, since, when fused in the outer flame of the blow-pipe, with a substance containing. manganese, it produces a green opaque bead, owing to the formation of manganate of soda.

§ 81.

3. CYANIDE OF POTASSIUM. (K Cy).

For the preparation of this reagent, vide § 42.

Uses.—Cyanide of potassium is an exceedingly powerful reducing agent in the dry way, in fact, it excels in its action almost all other reagents of the same class, and separates the metals not only from oxygen compounds, but also from sulphur compounds; this reduction is attended, in the first case, with formation of cyanate of potassa, the cyanide of potassium absorbing oxygen, and, in the latter case, with formation of sulphocyanide of potassium. By means of this reagent we may effect the reduction of metals from their compounds with the greatest possible facility; thus we may, for instance, produce pure antimony from antimonious acid or from sulphuret of antimony, metallic iron from peroxide of iron, &c., &c. The readiness with which cyanide of potassium enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit-lamp. Cyanide of potassium is a most valuable and important agent to

effect the reduction of arsenites and arseniates, and more par-
ticularly of sulpharsenious acid.   Compare § 95, *d.* 10.   Cyanide
of potassium is equally important as a blow-pipe reagent.   Its
action is exceedingly energetic ; substances like peroxide of tin,
bisulphuret of tin, &c., the reduction of which, by means of
carbonate of soda, requires a tolerably strong flame, are reduced
by cyanide of potassium with the greatest facility.   In blow-pipe
experiments, we invariably use a mixture of equal parts of car-
bonate of soda and cyanide of potassium ; the admixture of
carbonate of soda is intended to check in some measure the ex-
cessive fusibility of the cyanide of potassium.   This mixture of
cyanide of potassium, with carbonate of soda, besides being a far
more powerful reducing agent than the simple carbonate of soda,
has moreover this great advantage over the latter, that it is ab-
sorbed by the pores of the charcoal with extreme facility, and
thus permits the production of the metallic globules in a state of
the greatest purity.

<div align="center">§ 82.</div>

4. BIBORATE OF SODA.   (BORAX.)   (Na O, 2 B O$_3$)

The purity of commercial borax may be tested by dissolving
it, and adding to the solution either carbonate of potassa, solu-
tion of nitrate of baryta, or of nitrate of silver ; the addition of
either of the two latter reagents is to be preceded by that of
nitric acid.   The borax may be considered pure if these reagents
fail to produce any alteration in the solution ; but if either of
them cause the formation of a precipitate, or render the fluid
turbid, recrystallization will be necessary.   The pure borax is
exposed to a gentle heat, in a platinum crucible, until it ceases
to swell ; when cool it is powdered and kept for use.

Uses.—Boracic acid manifests a great affinity for oxides, when
brought into contact with them, in a state of fusion.   This affinity
enables it, in the first place, to combine directly with oxides ;
2, to expel weaker acids from their salts ; and 3, to predispose
metals, sulphur, &c., and haloid compounds to oxidize in
the outer flame of the blow-pipe, in order to combine with

the oxides.   Most of the thus produced borates fuse readily,
even without the aid of a flux, but far more so in conjunc-
tion with borate of soda; the latter salt acts in this ope-
ration either as a mere flux, or its action results in the forma-
tion of double salts.—Now, in the biborate of soda, we have both
free boracic acid and borate of soda; the union of these two
substances renders it one of our most important blow-pipe
reagents.   In the process of fluxing with borax, we usually select
platinum wire for a support; the loop of the wire is ignited,
dipped into the powder, and then exposed to the outer
flame; a colourless bead of fused borax is thus produced.   A
small portion of the substance under examination is then
attached to the borax bead, by bringing the latter into contact
with it, either whilst still hot, or having previously moistened it.
The bead with the sample of the substance intended for analysis
thus adhering to it is now again exposed, first to the flame of a
spirit-lamp, and finally to the blow-pipe flame, and the pheno-
mena to the manifestation of which this process gives rise, are
carefully observed and examined.   The following points ought to
be more particularly watched : 1. Whether or not the sample under
examination dissolves transparent, and whether or not it retains
this transparency on cooling; 2. whether the button exhibits a
distinct and definite color; since this, in many instances, at once
clearly indicates the individual metal which the analysed com-
pound contains; such is the case, for instance, with cobalt; and
3 whether the button manifests the same or a different deport-
ment in the outer or inner flame.   Phenomena of the latter kind
arise from the ensuing reduction of higher to lower oxides, or
even to the metallic state, and are for some substances particu-
larly characteristic.

§ 83.

5. PHOSPHATE OF SODA AND AMMONIA.   (MICROCOSMIC SALT).

$(P\,O_5,\ Na\,O,\ N\,H_4\,O,\ H\,O)$.
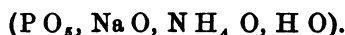
Preparation.—Dissolve six parts of phosphate of soda and one
part of pure chloride of ammonium in two parts of hot water, and

allow the solution to cool. Free the thus produced crystals of the double phosphate of soda and ammonia by recrystallization from the chloride of sodium which adheres to them. Dry the purified crystals, and powder them for use.

Uses.—When phosphate of soda and ammonia is subjected to the action of heat, the ammonia escapes with the water of crystallization, and a compound of similar composition to borax remains, viz., a compound which contains both a free acid and a readily fusible salt. The action of microcosmic salt is therefore analogous to that of biborate of soda. We prefer it, however, in some cases to borax, as a solvent or flux, the beads which it forms with many substances being more beautifully and distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with microcosmic salt; the loop of the wire must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed in the preceding paragraph.

§ 84.

6. PROTONITRATE OF COBALT. $(Co\,O,\,N\,O_5)$.

Preparation.—An intimate mixture of two parts of very finely powdered cobalt ore, four parts of nitrate of potassa, one part of effloresced carbonate of soda, and one part of dry carbonate of potassa, is gradually projected into a red-hot crucible; the latter is exposed to the strongest possible heat, until the mass becomes of a pasty consistence. When cool, it is powdered and boiled with water; the impure peroxide of cobalt thus produced is thoroughly washed, and afterwards digested and heated with hydrochloric acid until dissolved. The solution, which is of a dark green color, and generally gelatinous, owing to the separation of silicic acid—is evaporated to dryness. After treating the residue with hydrochloric acid, water is added, and the whole warmed until the metallic oxides are dissolved; when cool, a solution of carbonate of ammonia is first added, until the formation of a precipitate commences, and afterwards carbonate of baryta. Allow it to stand some time, then filter and well wash the precipitate, which contains all the iron as oxide: add hydrochloric acid to the

filtrate, and saturate with chlorine gas; now add carbonate of soda until the free acid is almost neutralized, and then an excess of carbonate of baryta. After twelve hours it is filtered, and the precipitate which contains all the cobalt as peroxide is well washed, dissolved in hydrochloric acid, the baryta thrown down by means of sulphuric acid, and after separating the sulphate of baryta the cobalt is precipitated by carbonate of soda.

Uses.—The protoxide of cobalt, when ignited with certain infusible substances, forms with the latter peculiarly-colored compounds. The process of ignition is conducted in the following manner. A sample of the finely-powdered substance under examination is ignited on a charcoal support, a drop of solution of protonitrate of cobalt is added, and the substance again ignited. In this process, oxide of zinc acquires an intensely green color, alumina a blue, and magnesia a faint rosy tint. The rose tint of magnesia is so slight that beginners frequently overlook this reaction. Silica likewise acquires a faint blue tint when ignited after previous moistening with solution of protonitrate of cobalt; this ought to be borne in mind when testing for alumina. The blue color of the alumina compound is, however, far more beautiful and intense than that of the silica compound.

SECTION III.

ON THE DEPORTMENT OF THE VARIOUS SUB-STANCES WITH REAGENTS.

§ 85.

I stated in my introductory remarks that the operations and experiments of qualitative analysis have for their object the conversion of the *unknown* constituents of any given compound into forms of which we *know* the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the individual constituents of which the

analysed compound consists.   The greater or less value of such
analytical experiments, like that of all other inquiries and inves-
tigations, depends entirely upon the greater or less degree of
certainty with which they lead to definite results, no matter
whether of a positive or negative nature.   But as a question does
not render us a whit the wiser if we do not know the lan-
guage in which the answer is returned, so, in like manner, will
analytical investigations prove unavailing if we do not under-
stand the mode of expression in which the desired information
is conveyed to us ; in other words, if we do not know how to
interpret the phenomena produced by the action of our reagents
upon the examined substance.

Before therefore we can proceed to enter upon the practical
investigations of analytical chemistry, it is indispensable that
we should *really* possess the most perfect knowledge of the
deportment, relations, and ,properties of the new forms into
which we intend to convert the substances which we wish to
analyse.   Now, this perfect knowledge consists, in the first place,
in a clear conception and comprehension of the conditions ne-
cessary for the formation of the new compounds, and for the
manifestation of the various reactions in general ; and, in the
second place, in a distinct impression of the color, form, and
physical properties which characterize the new compound.   This
section of the work demands, therefore, not simply the most
careful and attentive study, but requires, moreover, that the stu-
dent should *examine and verify, by actual experiment, every
fact asserted in it.*   The method usually adopted in elementary
works on chemistry is, to treat of the various substances and
their behaviour with reagents individually and separately, and to
point out their characteristic reactions.   I have, however, in the
present work, deemed it more judicious and better adapted to its
elementary character, to arrange those substances which are in
many respects analogous, into groups, and thus, by confronting
their analogies with their differences, to place the latter in the
clearest possible light.

A.—DEPORTMENT AND PROPERTIES OF THE METALLIC OXIDES.

§ 86.

First Group.

POTASSA, SODA, AMMONIA.

Properties of the Group.—The alkalies are readily soluble in water in their pure, or caustic state, and likewise as sulphurets and carbonates. They do not, therefore, precipitate one another in either state, nor are they precipitated by sulphuretted hydrogen under any condition whatever. The solutions of the pure alkalies, as well as of their sulphurets and carbonates, restore the blue color of reddened litmus paper, and impart an intense brown tint to turmeric paper.

Special reactions.

a. POTASSA. $(K\ O)$.

1. The heat of a spirit-lamp fails to volatilize potassa, its hydrate and salts. Potassa and its hydrate deliquesce in the air; the oily liquids which they thus form do not solidify by absorption of carbonic acid.

2. Nearly the whole of the salts of potassa are readily soluble in water. They are colorless, provided the constituent acid be so. The neutral salts of potassa with strong acids do not alter vegetable colors. Carbonate of potassa crystallizes with difficulty, and deliquesces in the air. Sulphate of potassa is anhydrous, and suffers no alteration in the air.

3. *Bichloride of platinum* produces in the neutral and acid solutions of the salts of potassa a yellow crystalline heavy precipitate of CHLORIDE OF PLATINUM AND POTASSIUM.

$(K\ Cl,\ P\ Cl_2)$.

In concentrated solutions, this precipitate separates immediately upon the addition of the reagent, whilst, in dilute solutions, it forms only after some time. The presence of free hydrochloric acid promotes the formation of this precipitate. It

is difficultly soluble in water, and wholly insoluble in alcohol. Bichloride of platinum is, therefore, a particularly delicate test for salts of potassa. The best method of applying this re-agent is, to evaporate the aqueous solution of the potassa salt, with bichloride of platinum, to dryness in the water-bath. The residue is treated with alcohol and a few drops of water; under these circumstances the potassio-chloride of platinum re-mains behind as a heavy yellow crystalline powder. Care must be taken not to confound this double salt with ammonio-chloride of platinum, which greatly resembles it. (Vide § 86, *c.* 4.)

4. *Tartaric acid* produces in neutral or alkaline solutions of potassa salts—(in the latter case the reagent is to be added until the fluid acquires a strongly acid reaction)—a white, quickly sub-siding, *granular* crystalline precipitate of BITARTRATE OF POTASSA. $(K O, \overline{T} + H O, \overline{T}.)$ In concentrated solutions, this precipitate separates immediately; in dilute solutions, frequently only after the lapse of some time. Violent agitation of the fluid promotes its formation considerably. Free alkalies and free mineral acids dissolve the precipitate; it is difficultly soluble in cold, but readily soluble in hot water. Acid solutions must first be neutralized with solution of soda or carbonate of soda, before they can be tested for potassa with tartaric acid.

5. When salts of potassa are placed, by means of a platinum wire, in the apex of the inner *blow-pipe flame,* the outer flame ac-quires a VIOLET color; this arises from reduction of the potassa and subsequent re-oxidation of the reduced potassium. The tint which phosphate and borate of potassa imparts to the outer blow-pipe flame is scarcely perceptible. Presence of soda obscures this reaction completely.

6. When a salt of potassa is heated with a small quantity of water, alcohol added, and the latter ignited, the flame appears VIOLET. The presence of soda obscures this reaction also.

b. SODA. (Na O).

1. Soda, its hydrate, and salts, present in general the same

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deportment and properties as potassa and its corresponding com-
pounds.   The oily fluid which soda forms upon its deliquescence
in the air, re-solidifies speedily by absorption of carbonic acid.
Carbonate of soda crystallizes readily, and effloresces rapidly when
exposed to the air.   The same applies to sulphate of soda.

2. *Antimoniate of potassa* produces in neutral or alkaline solu-
tions of salts of soda a white crystalline precipitate of ANTIMO-
NIATE OF SODA. (Na O, Sb O$_s$).

When the solutions are concentrated, this precipitate is formed
immediately; but if dilute it separates only after the lapse of
some time.   Violent agitation of the mixture promotes the sepa-
ration of the precipitate.   If the fluid, after the addition of the
reagent, be stirred with a glass rod, moving the latter along
the sides of the vessel, the lines described, will, even in very
dilute solutions, become visible, since the precipitate commences
to form at those parts that have been touched by the rod.   The
presence of neutral salts of potassa does not interfere with
the formation of the precipitate.   Carbonate of potassa, how-
ever, prevents its separation wholly or partially, according to
the greater or less proportion in which it is present.   In cases,
therefore, where the solution under examination contains this
salt, it is necessary to precede the application of the anti-
moniate of potassa by the addition of hydrochloric or acetic acid
until the reaction of the solution remains only feebly alkaline.
Acid solutions require first to be neutralized with potassa,
since otherwise the reagent would suffer decomposition, and
hydrated antimonic acid or biantimoniate of potassa be preci-
pitated from it.

3. Salts of soda, when exposed on a platinum wire to the inner
blow-pipe flame, color the outer flame INTENSELY YELLOW, owing
to reduction of the soda and subsequent reoxidation of the reduced
sodium.   This reaction remains clearly perceptible, although the
soda contain a considerable admixture of potassa.

4. When the salt of soda is heated with a small quantity of water,
alcohol added, and the latter ignited, the flame appears strongly
YELLOW.   The presence of a salt of potassa does not impair the
distinctness of this reaction.

5. *Bichloride of platinum* produces no precipitate in solutions of salts of soda: *tartaric acid* only when they are highly concentrated. The BITARTRATE OF SODA, which, in such cases, crystallizes out after the lapse of some time, appears invariably in the shape of small needles and columns, and not, like the corresponding salt of potassa, in the form of a granular crystalline precipitate.

c. AMMONIA. $(N\,H_4\,O)$.

1. Pure ammonia is gaseous at the common temperature; but we have most frequently to deal with it in its aqueous solution, in which it may be at once detected by its penetrating odor. It is expelled from its solution in water by the application of heat.

2. All the salts of ammonia are volatile at a high temperature, either with or without decomposition. Most of them are readily soluble in water. These solutions are colorless. The neutral compounds of ammonia with strong acids do not alter vegetable colors.

3. When salts of ammonia are triturated with *hydrate of lime,*—(but with the addition of a few drops of water,)—or are, either in solid form or in solution, heated with caustic potassa, the ammonia is liberated in its gaseous state, and manifests itself, 1, by its characteristic *odor:* 2, by its *reaction* on moistened test-papers; and 3, by giving rise to the formation of *white fumes,* when any object (e. g. a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought into contact with it. These fumes arise from the formation of solid ammoniacal salts. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, admits less readily of mistake.

4. *Bichloride of platinum* manifests the same deportment with salts of ammonia as with salts of potassa; the yellow precipitate of CHLORIDE OF PLATINUM AND AMMONIUM $(N\,H_4\,Cl,\,Pt\,Cl_2)$ is, however, of a somewhat lighter color than potassio-chloride of platinum.

5. *Tartaric acid* produces in solutions of salts of ammonia a precipitate of BITARTRATE OF AMMONIA, $(N\,H_4\,O,\,\overline{T}+H\,O,\,\overline{T})$.

This precipitate is formed in the same manner, and under the same circumstances, as the corresponding salt of potassa, but is somewhat more readily soluble than the latter.

Recapitulation and remarks.—The salts of potassa and soda are not volatile at a common red heat, whilst the salts of ammonia volatilize readily ; the latter may therefore be easily separated from the former by ignition.—The expulsion of ammonia from its compounds, by potassa or lime, affords the surest means of ascertaining the presence of this substance. Salts of potassa can be detected *positively*, only after the removal of the ammoniacal salts which may be present, since both these substances manifest the same or a similar deportment with bichloride of platinum and tartaric acid.—After the removal of the ammonia, the potassa is clearly and positively characterized by either of these two reagents. The most simple way of detecting the potassa in the potassio-chloride of platinum and bitartrate of potassa, is to decompose these salts by ignition. The ignited potassio-chloride of platinum yields the potassa in the form of chloride of potassium; the ignited bitartrate yields it in the form of carbonate of potassa. With respect to soda, antimoniate of potassa has now been added to the hitherto exceedingly limited means of positive detection of this substance, (such as the form of the crystals, and the general deportment and properties of some of its salts, and the yellow tint which its salts impart to the blow-pipe flame and to the flame of alcohol.) This reagent, however, effects the desired object only when applied with a careful and attentive consideration of the attendant circumstances. The most indispensable condition of its applicability is, that besides soda or potassa, no other bases be present in the solution, since the salts of the heavy metallic oxides, those of the earths and alkaline earths, and finally those of ammonia, are also precipitated by antimoniate of potassa.

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§ 87.

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

Properties of the group.—The alkaline earths are soluble in water in their pure (caustic) state, and as sulphurets. (Magnesia, however, dissolves but very sparingly in water.) These solutions manifest an alkaline reaction; with magnesia this is most clearly shown when placed upon moistened test-paper. The neutral carbonates and phosphates of the alkaline earths are insoluble in water. The solutions of their salts are, consequently, precipitated by alkaline carbonates and phosphates, but not by sulphuretted hydrogen under any condition. This deportment distinguishes the oxides of the second group from those of the first. The alkaline earths and their salts are non-volatile and colorless.

Special Reactions.

a. BARYTA. (Ba O).

1. Caustic baryta is pretty readily soluble in hot water, but rather difficultly so in cold water; it dissolves easily in dilute hydrochloric or nitric acids. Hydrate of baryta does not lose its water, upon ignition.

2. Most of the salts of baryta are insoluble in water. The soluble salts do not affect vegetable colors, and are decomposed upon ignition, with the exception of chloride of barium. The insoluble salts dissolve in hydrochloric acid, except the sulphate of baryta.—Nitrate of baryta and chloride of barium are insoluble in alcohol, and do not deliquesce in the air.

3. *Ammonia* produces no precipitate in the solutions of salts of baryta; *potassa* (free from carbonic acid) only in highly concentrated solutions. Water redissolves the bulky precipitate of CRYSTALS OF BARYTA (Ba O, H O + 9 aq.) produced by potassa.

4. *Alkaline carbonates* throw down from solutions of baryta CARBONATE OF BARYTA, (Ba O, CO_2,) in the form of a white precipitate. In acid solutions, however, complete precipitation takes place only upon heating the fluid; the same is the case when

carbonate of ammonia is used as the precipitant. The presence of salts of ammonia does not interfere with the formation of the precipitate.

5. *Sulphuric acid,* and all the soluble *sulphates,* immediately produce, even in the most highly dilute solutions of baryta, a fine white precipitate of SULPHATE OF BARYTA, (Ba O, S O_3), which is insoluble in acids and alkalies.

6. *Hydrofluosilicic acid* throws down from solutions of baryta SILICOFLUORIDE OF BARIUM, (Ba Fl + Si Fl_2), in the form of a colorless, crystalline, quickly subsiding precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; it is nearly insoluble in hydrochloric and nitric acids.

7. *Phosphate of soda* produces in neutral or alkaline solutions of baryta, a white precipitate of PHOSPHATE OF BARYTA, (P O_5, 2 Ba O, H O), which is soluble in free acids. Addition of ammonia does not increase the quantity of this precipitate, nor does it promote its formation.

8. *Oxalic acid* produces only in concentrated solutions of baryta a white precipitate of OXALATE OF BARYTA, (Ba O, $\overline{O}$), which is soluble in acids. Addition of ammonia renders this reaction far more delicate, and it is only in highly dilute solutions that the joint action of oxalic acid and ammonia fails to produce a precipitate.

9. *Chromate of potassa* with a neutral solution of baryta salts causes a bright yellow precipitate (Ba O, Cr O_3) even if it be very dilute; this precipitate is soluble in hydrochloric or nitric acids but insoluble in acetic acid. If chromate of potassa be added to a solution of baryta containing free hydrochloric acid, the solution remains clear, but on the addition of acetate of potassa a yellow precipitate of chromate of baryta separates.

10. Salts of baryta, when heated with diluted *spirit of wine,* impart to the flame of the latter a YELLOWISH color, not, however, very characteristic.

b. STRONTIA. (Sr O).

1. Strontia, its hydrate, and salts, manifest nearly the same general deportment and properties as baryta and its correspond-

ing compounds.—Hydrate of strontia is more difficultly soluble in water than hydrate of baryta,—Chloride of strontium dissolves in absolute alcohol, nitrate of strontia is soluble in dilute alcohol; neither of the two latter compounds deliquesce in the air.

2. The salts of strontia manifest with *ammonia* and *potassa*, and also with the *alkaline carbonates* and with *phosphate of soda*, the same deportment as the salts of baryta.

3. *Sulphuric acid* and *sulphates* precipitate from solutions of strontia, SULPHATE OF STRONTIA, (Sr O, S O$_3$), in the form of a white powder, which is insoluble in acids and alkalies. Sulphate of strontia is far more soluble in water than sulphate of baryta; owing to this solubility, the precipitated sulphate of strontia separates from rather dilute solutions in general only after the lapse of some time; and this is invariably the case (even in concentrated solutions) if *solution of sulphate of lime* is used as the precipitant.

4. *Hydrofluosilicic acid* fails to produce any precipitate, even in concentrated solutions of strontia.

5. *Oxalic acid* precipitates even from tolerably dilute solutions ; after the lapse of some time, OXALATE OF STRONTIA, (Sr O, $\bar{\text{O}}$), in the form of a white powder. Addition of ammonia promotes the formation of the precipitate greatly, and increases its quantity considerably.

6. *Chromate of potassa* causes in concentrated solutions of salts of strontia a bright yellow precipitate, (Sr O, Cr O$_3$), but in dilute solutions, or such as contain free acetic acid, no change occurs.

7. If salts of strontia, which are soluble in water or alcohol, be heated with dilute alcohol, and the latter be ignited, the flame will appear of an intense CARMINE RED color, more particularly upon stirring the alcoholic mixture. This color must not be confounded with that which salts of lime impart to the flame of alcohol.

c. LIME. (Ca O).

I. Lime, its hydrate and salts, present, in their general deportment and properties, a great similarity to baryta and strontia and their corresponding compounds. Hydrate of lime is

far more difficultly soluble in water than the hydrates of baryta and strontia; it dissolves, besides, more sparingly in hot than in cold water. Hydrate of lime loses its water upon ignition. Chloride of calcium and nitrate of lime are soluble in absolute alcohol, and deliquesce in the air.

2. *Ammonia, potassa, alkaline carbonates,* and *phosphate of soda,* present the same deportment with salts of lime as with salts of baryta.

3. *Sulphuric acid* and *sulphate of soda* produce immediately in highly concentrated solutions of lime, white precipitates of SULPHATE OF LIME, $(Ca\ O,\ S\ O_3)$, which redissolve completely in a large amount of water, and are still far more soluble in acids. When less concentrated, the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in highly dilute solutions. Solution of sulphate of lime, of course, cannot produce a precipitate in salts of lime; and even a cold saturated solution of sulphate of potassa, mixed with an equal amount of water, fails to produce a precipitate, at least immediately. In solutions of lime, which are so highly dilute, that sulphuric acid has no apparent action on them, a precipitate will immediately form upon the addition of alcohol with the sulphuric acid.

4. *Hydrofluosilicic acid* and *neutral chromate of potassa* do not precipitate salts of lime.

5. *Oxalic acid* produces a white precipitate of OXALATE OF LIME, $(Ca,\ \overline{O})$, even in highly dilute neutral solutions of lime. Addition of ammonia promotes the formation of this precipitate, and increases its quantity. Oxalate of lime is readily soluble in hydrochloric and nitric acids, but not perceptibly so in acetic acid, nor in oxalic acid.

6. Soluble salts of lime, when heated with dilute *alcohol,* impart to the flame of the latter a YELLOWISH RED color, which is often confounded with that communicated to the flame of alcohol by salts of strontia.

d. MAGNESIA. (Mg O).

1. Magnesia and its hydrate are white powders of far greater

bulk than baryta, strontia and lime, and their hydrates. Magnesia and hydrate of magnesia are nearly insoluble both in cold and hot water. Hydrate of magnesia loses its water upon ignition.

2. Some of the salts of magnesia are soluble in water, the rest are insoluble. The soluble salts of magnesia have a nauseous, bitter taste; they do not alter vegetable colors, when in a neutral state; with the exception of sulphate of magnesia, they undergo decomposition, when ignited, and the greater part of them even upon simple evaporation of their solutions. All the salts of magnesia which are insoluble in water, dissolve in hydrochloric acid.

3. *Ammonia* throws down from the solution of neutral salts of magnesia, a part of the magnesia as HYDRATE, (Mg O, H O), in the form of a white bulky precipitate. The rest of the magnesia remains in solution as a double salt, viz. in combination with the ammoniacal salt which forms upon the decomposition of the salts of magnesia; these double salts of ammonia and magnesia are not decomposable by ammonia. It is owing to this tendency of salts of magnesia to form such double salts with ammoniacal compounds, that ammonia fails to precipitate them in presence of ammoniacal salts, or, what comes to the same point, that ammonia produces no precipitate in acid solutions of magnesia; and that precipitates produced by ammonia in neutral solutions of magnesia, are re-dissolved upon the addition of an ammoniacal salt.

4. *Potassa* and *caustic baryta* throw down, from solutions of magnesia, HYDRATE OF MAGNESIA. The separation of this precipitate greatly promoted by boiling the mixture. Salts of ammonia dissolve the precipitated hydrate of magnesia, and prevent its formation altogether when added in sufficient quantity to the magnesia solution, previously to the addition of the precipitant. If the solution be subsequently boiled, however, with an excess of potassa, the precipitate will of course make its appearance, since this process causes the decomposition of the ammoniacal salt and subsequent expulsion of the ammonia, removing thus the agent which retained the hydrate of magnesia in solution.

5. *Carbonate of potassa* produces in neutral solutions of magnesia a white precipitate of BASIC CARBONATE OF MAGNESIA. 3 (Mg O, C O$_2$ + aq) + Mg O, H O. One fourth of the carbonic acid of the carbonate of potassa is liberated upon the decomposition of this salt, and combines with a portion of the new-formed carbonate of magnesia to bicarbonate which remains in solution. This carbonic acid escapes upon ebullition; the application of heat will therefore promote the separation, and increase the quantity of the precipitate. Salts of ammonia prevent this precipitation, and redissolve precipitates already formed.

6. *Carbonate of ammonia* causes a precipitate in a cold solution of a magnesia salt only after some time; on boiling, however, the magnesia is entirely thrown down, chloride of ammonium and other ammoniacal salts, if present in considerable quantities, entirely prevent the precipitation of magnesia by carbonate of ammonia.

7. *Phosphate of soda* precipitates from not *too* highly dilute solutions of magnesia, PHOSPHATE OF MAGNESIA, (PO$_5$, 2 Mg O, H O), as a white powder. The separation of the precipitate is greatly promoted by ebullition. If, however, previous to the addition of phosphate of soda, muriate of ammonia and ammonia, (the latter in excess,) be added, a white crystalline precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA (P O$_5$, 2 Mg O, N H$_4$ O) will separate, even though the solution be highly dilute, in the latter case the separation may be greatly promoted and accelerated by vigorous stirring with a glass rod; even should the solution be so extremely dilute as to forbid the formation of a precipitate; yet the lines of direction, in which the glass rod has moved along the sides of the vessel, will after the lapse of some time appear distinctly as white streaks. Pure water or solutions of the ammoniacal salts dissolve the precipitate but slightly; in acids, however, even acetic, it is readily soluble. In water containing free ammonia it is insoluble.

8. *Oxalate of ammonia* (but not free oxalic acid) produces a white precipitate of OXALATE OF MAGNESIA. (Mg O, $\overline{\text{O}}$). Salts of ammonia prevent its formation.

9. *Sulphuric acid, hydrofluosilicic acid,* and *chromate of potassa,* fail to precipitate salts of magnesia.

10. If magnesia, or a salt of magnesia, be moistened with solution of *protonitrate of cobalt*, and subsequently exposed upon a charcoal support to the continued action of a strong *blow-pipe flame*, a mass will be produced of a faint flesh tint, which becomes distinct only upon cooling, but is never very intense.

Recapitulation and remarks.—The difficult solubility of the hydrate of magnesia, the ready solubility of the sulphate, and the disposition of salts of magnesia to form double salts with ammoniacal compounds, are the three principal points in which magnesia differs from the other alkaline earths. We invariably select for its positive detection, the reaction with phosphate of soda, applied in conjunction with ammonia. Should baryta strontia, or lime be present, these earths are to be removed first, before proceeding to apply the special test for magnesia; this removal may be effected either by heating the fluid under examination with carbonate of ammonia with sal ammoniac, or by heating it with sulphate of potassa and oxalate of ammonia in conjunction with sal ammoniac. The detection of baryta is an easy task under any circumstances, since the precipitate of sulphate of baryta which separates from baryta solutions immediately upon the addition of solution of sulphate of lime, and the reaction of baryta with hydrofluosilicic acid are indubitable proofs of the presence of this earth. Strontia may likewise readily be detected by its deportment with solution of gypsum, provided, of course, no baryta be present. Should baryta be present, this substance is to be removed, before proceeding to test for the strontia. The separation of strontia from baryta is best effected by precipitating them as carbonates, dissolving in excess of acetic acid, adding chromate of potassa slightly in excess, boiling, and then filtering off the insoluble chromate of baryta. When testing for strontia by means of the alcohol flame, the operator must take care not to confound the color which strontia imparts to this flame with that communicated to it by salts of lime.—For the positive detection of

lime, we invariably select oxalate of ammonia. Before apply-
ing this test, however, baryta and strontia are to be removed,
since the deportment which these substances manifest with oxalic
acid is analogous to that presented by lime, differing from it
simply in intensity. The removal of baryta, and strontia is ef-
fected by means of sulphate of potassa. It may happen in this
process that a portion of the lime precipitates with the baryta
and strontia; this is, however, a matter of indifference, since
there remains always a sufficient amount of lime in solution to
permit the positive and indubitable detection of this substance
by oxalate of ammonia. The best way of effecting the detection
of the alkaline earths in their phosphates is to decompose them
by means of perchloride of iron in conjunction with acetate of
potassa, (vide § 99, a. 8.) The oxalates of the alkaline earths
are converted into carbonates by ignition preparatory to the
detection of the individual earths which they contain. Sulphate
of baryta and sulphate of strontia are fluxed with alkaline car-
bonates, for the purpose of detecting the baryta and strontia.
Compare § 98, 5.

§ 88.

Third Group.

ALUMINA.   OXIDE OF CHROMIUM.

Properties of the group.—Alumina and oxide of chromium are
insoluble in water, both in their pure state and as hydrates. They
form no neutral salts with carbonic acid. Their sulphurets can-
not be produced in the humid way. Sulphuretted hydrogen,
consequently, fails to precipitate solutions of alumina and of oxide
of chromium; hydrosulphuret of ammonia precipitates the hy-
drated oxides from these solutions. This deportment with hydro-
sulphuret of ammonia distinguishes the oxides of the third, from
those of the two preceding groups.

Special Reactions.

a. ALUMINA. (Al₂ O₃).

1. Alumina is non-volatile and colorless; the hydrate is also colorless. Alumina dissolves in acids slowly and with very great difficulty; the hydrate in an amorphous state is readily soluble in acids; but its crystals dissolve with very great difficulty in these menstrua. After previous ignition with alkalies, alumina is readily dissolved by acids.

2. The salts of alumina are colorless, and most of them are non-volatile; some of them are soluble, others insoluble. The soluble salts have a sweetish astringent taste, redden litmus paper, and lose their acids, upon ignition. The insoluble salts are dissolved by hydrochloric acid, with the exception of some natural compounds of alumina, which latter may be rendered soluble in acids, by ignition with carbonate of soda.

3. *Potassa* throws down from the solutions of alumina a bulky precipitate of HYDRATE OF ALUMINA, (Al O₃ 3 H O)ₓ which contains an admixture of potassa, and generally also of a basic salt, it redissolves readily and completely in an excess of the precipitant, from which solution it will precipitate again upon addition of chloride of ammonium, even in the cold; but more completely still upon heating the solution, (compare § 23.) The presence of salts of ammonia does not prevent this precipitation by potassa.

4. *Ammonia* also produces in solutions of alumina a precipitate of HYDRATE OF ALUMINA, containing an admixture of ammonia and a basic salt; and this precipitate is also redissolved by a very considerable excess of the precipitant; this re-solution, however, ensues only with more or less difficulty, according to the greater or less amount of ammoniacal salts which the solution of alumina may contain in admixture.

It is this deportment of ammonia and ammoniacal salts with alumina, which accounts for the complete precipitation of hydrate

of alumina from solution in potassa, by an excess of chloride of ammonium.

5. If alumina, or a compound of alumina, be ignited upon charcoal, before the blow-pipe, and afterwards moistened with a solution of *protonitrate of cobalt*, and then again strongly ignited, an unfused mass will be produced of a deep SKY-BLUE color, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candle-light it appears violet.

<center>b. OXIDE OF CHROMIUM.   ($Cr_2 O_3$).</center>

1. Oxide of chromium is a green, its hydrate a bluish-grey-green powder. Oxide of chromium occurs in two modifications, one of which is dissolved slowly by dilute acids, whilst the other is altogether insoluble in dilute acids, and dissolves but very slowly even in boiling concentrated sulphuric acid. The application of an intense heat causes the conversion of the soluble into the insoluble modification; this transformation is attended with vivid incandescence. Hydrated oxide of chromium is readily soluble in acids.

2. The two modifications of the oxide of chromium are found in its salts. The salts corresponding to the insoluble modification are of a bright violet color, and insoluble in water and acids; whilst those corresponding to the soluble modification are green, partly soluble and partly insoluble in water, but, without exception, soluble in hydrochloric acid.—Many of the green salts are converted into the insoluble modification by the action of heat; this transformation being attended with a change of color from green to violet; by fluxing in conjunction with carbonate of soda, these salts are re-converted into the soluble modification.—The solutions of the salts of oxide of chromium exhibit a highly characteristic, blackish green color, even though highly dilute. The solution of some of the double salts of oxide of chromium, such as sulphate of chromium and alumina, oxalate of chromium and potassa, &c., appear of a blackish violet color.—The soluble salts of oxide of chromium redden litmus;—those with volatile acids are decomposed upon ignition.

3. *Potassa* produces in solutions of oxide of chromium a bluish-green precipitate of HYDRATED OXIDE OF CHROMIUM, ($Cr_2 O_3$, 5 H O), which dissolves readily and completely in an excess of the precipitant, imparting an emerald-green tint to the fluid. Upon *long-continued* ebullition, the whole of the hydrated oxide will again separate, and the supernatant fluid will then appear perfectly colorless. The same re-precipitation will take place if chloride of ammonium be added to the solution in potassa, and the mixture subsequently heated.

4. *Ammonia* produces in solutions of oxides of chromium the same precipitate of HYDRATED OXIDE OF CHROMIUM as potassa; a small portion of these precipitates redissolves in an excess of the precipitant in the cold, imparting to the fluid a peach-blossom red-tint; but if, after the addition of the excess of ammonia, heat be applied to the mixture, the whole of the hydrated oxide of chromium will precipitate.

5. The fusion of oxide of chromium or of any of its compounds with a *mixture of nitrate of potassa and carbonate of soda*, invariably gives rise to the formation of an ALKALINE CHROMATE, part of the oxygen of the nitric acid separating from the nitrate of potassa, and converting the oxide of chromium into chromic acid, which combines with the potassa of the decomposed nitrate of potassa with the soda of the carbonate. For the deportment and properties of chromic acid, vide § 97. *b.*

6. *Phosphate of soda and ammonia* dissolves oxide of chromium and its salts both in the *oxidizing* and *reducing* flame of the blow-pipe, into clear beads of a faint YELLOW-GREEN tint, which, upon cooling, changes to EMERALD-GREEN. The oxide of chromium and its salts manifest a similar deportment with *borax.*

Recapitulation and remarks.—The solubility of the hydrates of alumina and oxide of chromium in potassa, and their re-precipitation by chloride of ammonium, enable us to effect, in the first place, the separation of alumina and oxide of chromium from the oxides of other groups, and, in the second place, the *individual* and *positive* detection of alumina, when oxide of chromium

is absent.   Should the latter substance be present—(which
will either appear at once from the color of the solution,
or may be readily ascertained, at all events, from the deport-
ment of the substance under examination when exposed to
the blow-pipe flame with microcosmic salt,)—it must first be
removed before the operator can proceed to test for alu-
mina.   The separation of oxide of chromium from alumina
may be effected completely, by fusing the mixed oxides with
nitre.   The precipitation of oxide of chromium, which ensues
upon long-continued ebullition of the solution of the oxide
in potassa, is generally sufficiently complete and accurate, but
in some cases gives rise to mistakes.   It is, moreover, finally
to be borne in mind, that alkalies produce no precipitates in the
solutions of alumina and oxide of chromium, when non-volatile
organic substances are present, such as sugar, tartaric acid, &c.,
&c.   It sometimes happens, that on heating alumina in a solution
of potassa with muriate of ammonia, in order to separate the two
bases, or by simply boiling if only chromium is present, they will
not separate at all, or only partially, on filtering; to obviate this
the solution must be acidified with hydrochloric acid, boiled some
time, whilst chlorate of potassa is gradually added, and then preci-
pitated with ammonia.

§ 89.

Fourth Group.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF
 NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—PER-
 OXIDE OF IRON.

Properties of the group.—The sulphurets corresponding with
the oxides of the fourth group are more or less soluble in dilute
acids, but insoluble in water, alkalies, and alkaline sulphurets.
Suphretted hydrogen fails, therefore, altogether to produce a pre-
cipitate in solutions of the salts of these oxides when these
solutions contain free acid ; neutral solutions are either not at all

or but imperfectly precipitated by this reagent; but alkaline solutions are completely precipitated by sulphuretted hydrogen. From neutral solutions of the salts of the oxides of this group the corresponding sulphurets will precipitate if an alkaline sulphuret be substituted for sulphuretted hydrogen.

Special Reactions.

a. OXIDE OF ZINC. (Zn O).

1. The oxide of zinc and its hydrate are white powders, which dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid. The oxide of zinc acquires a lemon-yellow tint when heated, but it reassumes its original white color upon cooling.

2. The compounds of oxide of zinc are colorless. Its soluble neutral salts redden litmus paper, and are readily decomposed by heat, with the exception of sulphate of zinc, which can bear a faint red heat, without undergoing decomposition.

3. *Sulphuretted hydrogen* precipitates from neutral solutions of salts of zinc a portion of this metal as white hydrated SULPHURET OF ZINC (Zn S). In acid solutions, this reagent fails altogether to produce a precipitate, if the free acid present is one of the stronger acids.

4 *Hydrosulphuret of ammonia* throws down from *neutral* as *sulphuretted hydrogen* does from *alkaline* solutions of salts of zinc, the whole of the metal as hydrated SULPHURET OF ZINC, in the form of a white precipitate. This precipitate is not redissolved by an excess of hydrosulphuret of ammonia, nor by potassa or ammonia; but it dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid. It is almost insoluble in acetic acid.

5. *Potassa and ammonia* throw down from solutions of salts of ZINC, HYDRATED OXIDE OF ZINC (Zn O, H O) in the form of a white gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant.

6. *Carbonate of potassa* produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC (3 [Zn O, H O]+2 [Zn O, C O$_2$]) which is insoluble in an excess of the precipitant. The presence of salts of ammonia prevents the formation of

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this precipitate, and the addition of such salts causes the re-solution of precipitates already formed, owing to the ammoniacal salts combining with the oxide of zinc to soluble double salts of oxide of zinc and ammonia.

7. *Carbonate of ammonia* also produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC, but this precipitate redissolves upon further addition of the precipitant.

8. When the mixture of oxide of zinc, or one of its salts with *carbonate of soda* is exposed to the *reducing flame* of the blow-pipe, the charcoal support becomes covered with a slight incrustation of OXIDE OF ZINC, which presents a yellow color whilst hot, and turns white upon cooling. This incrustation is caused by the reduced metallic zinc volatilizing at the moment of its reduction, and reoxidizing in passing through the outer flame.

9. If oxide of zinc, or one of the salts of zinc, be moistened with solution of *protonitrate of cobalt*, and subsequently heated before the blow-pipe, an unfused mass will be obtained, of a beautiful GREEN color; this mass is a compound of oxide of zinc with protoxide of cobalt.

b. PROTOXIDE OF MANGANESE. (Mn O).

1. Protoxide of manganese exhibits a grey-greenish color; the hydrated protoxide is white. Both the protoxide and its hydrate are peroxidized, and turn brown, when exposed to the air. They are readily soluble in hydrochloric acid, nitric acid, and sulphuric acid.

2. The protosalts of manganese are colorless or of a pale red color; some of them are soluble, others insoluble. The soluble salts, with the exception of protosulphate, are readily decomposed by a red-heat. The solutions of the soluble protosalts of manganese do not alter vegetable colors.

3. *Sulphuretted hydrogen* fails to precipitate acid solutions of protosalts of manganese; neutral solutions, this reagent precipitates *but very imperfectly.*

4. *Hydrosulphuret of ammonia* throws down from neutral, as sulphuretted hydrogen does from alkaline, solutions of the proto-

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salts of manganese, the whole of this metal as hydrated SULPHURET OF MANGANESE (Mn S) in the form of a bright flesh-colored pre-cipitate, which turns dark-brown upon exposure to the air; this precipitate is insoluble in hydrosulphuret of ammonia and in alkalies, but readily soluble in hydrochloric, nitric, and acetic acids.

5. *Potassa* and *ammonia* produce whitish precipitates of HY-DRATED PROTOXIDE OF MANGANESE (Mn O, H O), which, upon exposure to the air, speedily acquire a brownish, and, finally, a deep blackish-brown color, owing to the ensuing conversion of the hydrated protoxide into hydrated peroxide, by the absorption of oxygen from the air. Ammonia and carbonate of ammonia do not redissolve this precipitate, but the presence of sal am-moniac prevents the precipitation by ammonia altogether, and that by potassa partly. Solution of sal ammoniac redissolves only those parts of *already formed* precipitates which have not yet undergone peroxidation. The solution of the hydrated pro-toxide of manganese in sal ammoniac is entirely owing to the disposition of the protosalts of manganese to form double salts with salts of ammonia. Pellucid solutions of double salts of manganese and ammonia turn brown, when exposed to the air, and deposit dark-brown hydrated peroxide of manganese. (Mn$_2$ O$_3$, 2 HO).

6. If any of the compounds of manganese be fused with *carbonate of soda*, in the *outer* flame of the blowpipe, upon a platinum wire, MANGANATE OF SODA (Na O, Mn O$_3$) will be formed, which will make the fused mass appear GREEN while hot, and of a BLUE-GREEN tint after cooling, the bead at the same time becoming turbid. This reaction enables us to detect the smallest quantities of manganese. The delicacy of the test may be still further increased by the addition of a minute quantity of nitrate of potassa to the carbonate of soda.

7. *Borax* and *phosphate of soda and ammonia* dissolve man-ganese compounds, in the *outer* flame of the blow-pipe, into clear VIOLET-RED beads, which, upon cooling, acquire an AMETHYST-RED tint; they lose their color in the *inner* flame, owing to an ensuing reduction of the peroxide to protoxide. The

bead which borax forms with manganese, appears black when containing a considerable portion of peroxide of manganese, but that formed by phosphate of soda and ammonia never loses its transparency. The latter loses its color, in the inner flame of the blow-pipe, far more readily than the former.

c. PROTOXIDE OF NICKEL. (Ni O).

1. Protoxide of nickel is a grey, its hydrate a green powder. Both the protoxide and its hydrate are unalterable in the air, and readily soluble in hydrochloric acid, nitric acid, and sulphuric acid.

2. The protosalts of nickel are in their anhydrous state, for the most part yellow, and in their hydrated state, green; their solutions are of a light green color. The soluble neutral salts redden litmus paper, and are decomposed at a red-heat.

3. *Sulphuretted hydrogen* fails to precipitate solutions of salts of nickel containing free mineral acid; in neutral solutions this reagent precipitates *them but very imperfectly.*

4. *Hydrosuphuret of ammonia* produces in neutral, as sulphuretted hydrogen does in alkaline solutions of protosalts of nickel, a black precipitate of hydrated SULPHURET OF NICKEL, (Ni S), which is not altogether insoluble in hydrosulphuret of ammonia containing an admixture of free ammonia or of pentasulphuret of ammonium; it is owing to this slight solubility of the sulphuret of nickel in sulphuret of ammonium, that the fluid from which it has been thrown down exhibits, in most cases, a brownish color. Sulphuret of nickel dissolves with great difficulty in hydrochloric acid, slightly in acetic acid, but readily in aqua regia.

5. *Potassa* produces a light green precipitate of HYDRATED PROTOXIDE OF NICKEL, (Ni O, H O), which is insoluble in potassa, and unalterable in the air. Carbonate of ammonia dissolves this precipitate to a greenish-blue fluid, from which potassa reprecipitates the nickel, as a yellow-green hydrated protoxide of nickel.

6. *Ammonia* likewise produces a precipitate of HYDRATED PROT-

OXIDE OF NICKEL; but this redissolves readily in an excess of the precipitant as a double salt of protoxide of nickel and ammonia, the solution exhibiting a blue color. Potassa precipitates hydrated protoxide of nickel from this solution. Ammonia fails to produce a precipitate in solutions of protosalts of nickel which contain ammoniacal salts or free acid.

7. *Cyanide of potassium* produces a yellowish-green precipitate of CYANIDE OF NICKEL, (Ni Cy), which redissolves readily in an excess of precipitant as a double cyanide of nickel and potassium, (Ni Cy + K Cy). The solution exhibits a brownish yellow color. Upon adding sulphuric acid or hydrochloric acid to this solution, the cyanide of potassium is decomposed, and the cyanide of nickel re-precipitated; the latter substance is very difficultly soluble in an excess of the precipitant acid, in the cold, but readily so, upon boiling.

8. *Borax* and *phosphate of soda and ammonia* dissolve compounds of protoxide of nickel, in the *outer* flame of the blowpipe, to clear beads of a dark yellow color, with a shade of red-brown; upon cooling, they become lighter, and finally almost colorless. Addition of nitre or carbonate of potassa changes the color to blue or to a dark purple. The bead which phosphate of soda and ammonia forms with protosalts of nickel, remains unaltered in the *inner* flame of the blow-pipe, but that of borax turns grey and turbid from reduced metallic nickel.

d. PROTOXIDE OF COBALT. (Co O).

1. Protoxide of cobalt is a grey, its hydrate a pale red powder. Both the protoxide and its hydrate dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid.

2. The protosalts of cobalt are blue in their anhydrous, and of a characteristic bright red tint in their hydrated state. Their solutions show this color even though considerably diluted. The soluble neutral salts redden litmus paper, and are decomposed at a red heat.

3. *Sulphuretted hydrogen* fails to precipitate acid solutions of cobalt, and precipitates neutral solutions, but very incompletely, when they contain weak acids; the precipitates are of a black color.

4. *Hydrosulphuret of ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions of protosalts of cobalt, the whole of this metal as black hydrated SULPHURET OF COBALT. (Co S). This substance is insoluble in alkalies and hydrosulphuret of ammonia, difficultly soluble in hydrochloric acid, nearly insoluble in acetic acid, but readily so in aqua regia.

5. *Potassa* produces in solutions of cobalt BLUE precipitates of basic salts of cobalt, which turn GREEN upon exposure to the air, owing to the absorption of oxygen, and are, upon boiling, converted into the pale red hydrated protoxide of cobalt, which appears generally rather discolored from an admixture of peroxide formed in the process. These precipitates are insoluble in potassa; but neutral carbonate of ammonia dissolves them completely to intensely violet-red fluids, in which potassa produces but *very scanty* precipitates.

6. *Ammonia* produces the same precipitate as potassa, but this redissolves in an excess of the ammonia to a reddish-brown fluid, in which potassa produces, if any, a very slight precipitate. Ammonia fails to precipitate solutions of protosalts of cobalt containing ammoniacal salts or free acids.

7. The addition of *cyanide of potassium* to a solution of cobalt acidified with some hydrochloric acid, gives rise to the formation of a brownish white precipitate of PROTOCYANIDE OF COBALT, (Co Cy), which dissolves readily as a double cyanide of cobalt and potassium, ($Cy_6 Co_2$, 3 K=2 C Ky, 3 K), when heated with an excess of the precipitant, in presence of free hydrocyanic acid. Acids cause no precipitation in the solutions of this double salt.

8. *Borax* dissolves compounds of cobalt both in the *inner* and *outer* flame of the blow-pipe, into clear beads of a magnificent BLUE color, which verges almost upon black, when the cobalt is present in considerable proportion. This test is as delicate as it is characteristic. *Phosphate of soda and ammonia* manifests with salts of cobalt, before the blow-pipe, an analogous but less intense reaction.

e. PROTOXIDE OF IRON. (Fe O).

1. Protoxide of iron is a black powder; hydrated protoxide of

iron is white, in a moist state it absorbs oxygen, and turns speedily grey green, and finally becoming brown red; both the protoxide and its hydrate are readily soluble in hydrochloric acid, sulphuric acid, and nitric acid.

2. The protosalts of iron have a greenish color; their solutions appear colored only when quite concentrated. Exposed to the air, they absorb oxygen, and' become converted into salts of the ferroso-ferric oxide. The soluble neutral salts redden litmus paper, and are decomposed at a red heat.

3. Acid solutions are not precipitated by *sulphuretted hydrogen*, neutral solutions, with weak acids, *but incompletely ;* the precipitates are of a black color.

4. *Hydrosulphuret of ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions of protosalts of iron, the whole of this metal as black hydrated SULPHURET OF IRON, (Fe S), which is insoluble in alkalies and alkaline sulphurets, but readily soluble in hydrochloric acid and nitric acid as well as in acetic acid.

5. *Potassa* and *ammonia* produce a precipitate of HYDRATED PROTOXIDE OF IRON, (Fe O, H O), which, in the first moment, looks almost white, but acquires, after a very short time, a dirty green, and finally a reddish-brown color, owing to absorption of oxygen from the air. The presence of salts of ammonia prevents the precipitation by potassa partly, and that by ammonia altogether. If the alkaline solution of protoxide of iron, which is thus obtained by the agency of ammoniacal salts, be exposed to the air, hydrated peroxide of iron will precipitate.

6. *Ferrocyanide of potassium* produces in solutions of protoxide of iron a bluish-white precipitate of FERROCYANIDE OF POTASSIUM AND IRON, (2 Cfy, K, 3 Fe), which, by absorption of oxygen from the air, speedily acquires a blue color, the whole of the potassium, and one equivalent of iron of every three equivalents of the compound being oxidized, so as to leave two equivalents of Prussian blue (3 Cfy, 2 Fe₂) behind. Nitric acid or chlorine effect this oxidation immediately.

7. *Ferricyanide of potassium* produces a magnificently blue-colored precipitate of FERRICYANIDE OF IRON, (2 Cfy, 3 Fe).

This precipitate does not differ in color from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potassa. In highly dilute solutions of protosalts of iron, this ferricyanide of potassium produces simply a deep blue-green coloration.

8. *Sulphocyanide of potassium* does not alter solutions of protoxide of iron, free from admixture of peroxide.

9. *Borax* dissolves protosalts of iron in the *oxidizing* flame, forming DARK RED BEADS, the color of which changes to bottle green in the *inner* flame, owing to the reduction of the new-formed peroxide to magnetic-oxide. Both tints disappear totally, or in a great measure, upon cooling. *Phosphate of soda and ammonia* manifest a similar deportment with the protosalts of iron; the beads produced by the latter reagent lose their color, upon cooling, more completely still than in the case with those produced by borax.

f. PEROXIDE OF IRON. $(Fe_2 O_3)$.

1. Peroxide of iron is a more or less deep-colored red-brown powder; hydrated peroxide of iron has a somewhat lighter color. Both the protoxide and its hydrate dissolve in hydrochloric acid, nitric acid, and sulphuric acid; the hydrate dissolves readily in these acids, but the oxide dissolves with greater difficulty, especially after ignition.

2. The persalts of iron are of a more or less reddish yellow color. Their solutions exhibit this color even though highly diluted. The soluble neutral salts redden litmus paper, and are decomposed by heat.

3. *Sulphuretted hydrogen*, when added to a neutral or acid solution of a persalt of iron, decomposes it; the hydrogen reduces the persalt of iron to the state of a protosalt, by withdrawing from the peroxide of iron one-third of its oxygen, with which it forms water; part of the sulphur of the decomposed sulphuretted hydrogen separates in a highly-divided state, and imparts a TURBID and MILKY appearance to the fluid.

4. *Hydrosulphuret* of *ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions of persalts of

iron, the whole of this metal as black SULPHURET OF IRON, (Fe S). This precipitation is preceded by the reduction of the persalt to a protosalt. In very dilute solutions, the reagent produces only a blackish-green coloration. The minutely divided protosulphuret of iron subsides in such cases only after long standing. Sulphuret of iron, as already stated, (e. 4), is insoluble in alkalies and alka-line sulphurets, but readily soluble in hydrochloric acid, nitric acid, and also in acetic acid.

5. *Potassa* and *ammonia* produce bulky reddish-brown preci-pitates of HYDRATED PEROXIDE OF IRON, ($F_2 O_3$, H O), which are insoluble in an excess of the precipitant as well as in salts of am-monia.

6. *Ferrocyanide of potassium* produces, even in highly dilute solutions, a magnificently blue precipitate of SESQUIFERROCYANIDE OF IRON, (3 Cfy, 2 Fe_2), (Prussian blue), which is insoluble in hydrochloric acid, but is readily decomposed by potassa, with pre-cipitation of peroxide of iron.

7. *Ferricyanide of potassium* deepens the color of solutions of persalts of iron to a ruddy brown, but it fails to produce a preci-pitate.

8. *Sulphocyanide of potassium* imparts to neutral or acid solu-tions of persalts of iron an intensely blood-red color, arising from the formation of a soluble SULPHOCYANIDE OF IRON. This test is the most delicate of all; it will indicate the presence of peroxide of iron even in fluids which are so highly dilute that every other reagent fails to produce the slightest visible alteration. The red coloration may, in such cases, be detected most distinctly, by resting the test-tube upon a sheet of white paper, and looking into it at the top.

9. On the addition of carbonate of baryta in excess to a persalt of iron, carbonic acid is evolved, and the iron precipitated as a basic salt.

10. On nearly neutralising a solution of a persalt of iron with carbonate of soda, and heating with an excess of acetate of soda, all the iron will be precipitated as a basic salt. This, and the above-mentioned reaction (9), are of less value in detecting per-salt of iron than in separating them from other bases in this group.

11. The persalts of iron present the same deportment and phe-
nomena as the protosalts, when exposed to the action of the *blow-
pipe flame*, vide *e.* 9, (protoxide· of iron.)

Recapitulation and remarks.—On observing the behaviour of
the oxides of the fourth group with solution of potassa, the sepa-
ration of the oxide of zinc, which is soluble in an excess of this
reagent appears perfect; however, in carrying out these experi-
ments, we find that in the presence of peroxide of iron, protoxide
of cobalt, &c., if the proportion of these be large, some of the
oxide of zinc will be precipitated with them ; and if only a small
proportion of oxide of zinc be present, it frequently occurs that no
trace of this metal can be detected in the alkaline solution. Also
from the behaviour of the different oxides with sal ammoniac and
excess of ammonia, one would conclude that the separation of
peroxide of iron from cobalt, nickel, manganese, and also oxide of
zinc by this means, would be perfect ; it will, however, be found
that this is not quite correct, as in precipitating the iron from a
mixture of the different oxides, a small portion of the latter are
apt to separate with it, so that by this process traces of cobalt,
manganese, &c., may be overlooked. It is far better to separate the
oxides of this fourth group by carbonate of baryta, as in this case
the iron is precipitated free from zinc, manganese, and nickel, and
is contaminated only with a trace of protoxide of cobalt. Oxide
of manganese may be separated from oxides of cobalt, nickel, and
zinc, by heating the freshly-precipitated sulphurets with mode-
rately strong acetic acid, which, whilst leaving the last-mentioned
sulphurets unacted on, dissolves the sulphurets of manganese; then,
in precipitating the acetic acid solution with caustic potassa, the
smallest trace can be detected before the blow-pipe.

If we now treat the undissolved sulphuret with very dilute hy-
drochloric acid, the sulphuret of zinc will be dissolved, and almost
the whole of the sulphurets of cobalt and nickel remain unacted
on. The zinc solution must now be entirely freed from sulphu-
retted hydrogen by boiling, then treated with excess of caustic
potassa, and finally precipitated by sulphuretted hydrogen. Cobalt
may be readily detected even in the presence of nickel by treating

it with borax before the blow-pipe. It is not so easy to discover traces of nickel with cobalt. There are, however, two accurate methods of doing it. In the first of these, the hydrochloric acid solution is saturated with chlorine, the excess of acid nearly neutralized with carbonate of soda; and, lastly, carbonate of baryta is added in excess; the cobalt is by this means entirely precipitated as hydrated oxide, while the nickel remains dissolved; and after the separation of the baryta by sulphuric acid, the nickel may be thrown down with solution of potassa. The second method is by precipitating the nickel and cobalt as cyanides and dissolving in excess of cyanide of potassium. If to this hydro-chloric or dilute sulphuric acid be added and the solution boiled, the cyanide of nickel will be decomposed, whilst by the action of the hydrocyanic acid set free from the excess of cyanide of potas-sium, by the hydrochloric acid, the cyanide of cobalt dissolved in the cyanide of potassium (K Cy, Co Cy) is converted into cobalto-cyanide of potassium, which is not affected by acids, 2 (K Cy, Co Cy) + K Cy + Cy H = Co 2 Cy$_6$, 3 K + H.

     Whether this precipitate be cyanide of nickel or cobalticyanide of nickel, is quite immaterial as far as the *detection of nickel* is concerned: all we have to bear in mind is simply this, that no precipitate will form if cobalt alone be present in the solution, since cobalticyanide of potassium is not decomposed by hydro-chloric acid. In order to get at the composition of the various precipitates which are formed by hydrochloric acid in solution of the mixed cyanides of nickel and cobalt, and to comprehend the general process, of their formation, we have to assume and con-sider three special and distinct cases, differing from one another in the relative proportions of nickel and cobalt, which the solu-tions under examination respectively contain.

         1, Ni : Co : : 3 eq. : 2 eq.
         2, Ni : Co : : 3 eq. : 2 eq. + x
         3, Ni : Co : : 3 eq. + x : 2 eq.

The solution will, in the first case, contain one eq. of cobalticya-nide of potassium, (Cy$_6$ Co$_2$, 3 K), and 3 eq. of double cyanide of nickel and potassium, 3 (Ni Cy, K Cy); now upon the addition of hydrochloric acid in excess to this solution, the double cyanide

of nickel and potassium suffers decomposition, and the potassium of the cobalticyanide of potassium transposes with the nickel of the cyanide of nickel ; the products of this process of double decomposition and transposition are chloride of potassium, hydrocyanic acid, and cobalticyanide of nickel, (Cy_6 Co_2, 3 Ni), which latter separates in the form of a dirty green precipitate containing the *whole* of the nickel and cobalt present in the solution.—In the second case we obtain equally a precipitate of cobalticyanide of nickel, but this precipitate, though containing the whole of the *nickel*, does *not* contain *all* the *cobalt* of the solution, since the excess of cobalticyanide of potassium is not decomposed.—In the third case, we obtain a precipitate of cobalticyanide of nickel, which contains the *whole* of the *cobalt* and a *portion* of the *nickel*, mixed with insoluble cyanide of nickel which contains the rest of the nickel. The cobalticyanide of nickel has been formed here in the same manner as in the first case, whilst the cyanide of nickel owes its formation to the decomposition of the *excess* of the double cyanide of nickel and potassium. Hence it is evident, that the presence of nickel is indispensable to the formation of a precipitate, and consequently, that the production of a precipitate is the most positive proof of the presence of this metal.

Finally it is necessary to mention, that alkalies fail to precipitate the oxides of the fourth group in presence of non-volatile organic substances, (such as sugar, tartaric acid, &c.) We have already seen that the same applies to alumina and oxide of chromium.

<center>§ 90.</center>

<center>*Fifth Group.*</center>

OXIDE OF SILVER—PROTOXIDE OF MERCURY—PEROXIDE OF MERCURY—OXIDE OF LEAD—OXIDE OF BISMUTH—OXIDE OF COPPER—OXIDE OF CADMIUM.

Properties of the group.—The sulphurets corresponding with the oxides of this group, are insoluble both in dilute acids and in alkaline sulphurets ; nevertheless, with oxide of copper, this is comparative ; with peroxide of mercury, this is only partially

true. The solution of these oxides are completely precipitated by sulphuretted hydrogen, no matter whether their reaction be neutral, alkaline, or acid.

For the sake of greater clearness and simplicity, we divide the oxides of this group into two sections, and distinguish,

1. OXIDES PRECIPITABLE BY HYDROCHLORIC ACID, viz. : oxide of silver, protoxide of mercury, oxide of lead.

2. OXIDES NOT PRECIPITABLE BY HYDROCHLORIC ACID, viz. : peroxide of mercury, oxide of copper, oxide of bismuth, oxide of cadmium.

Lead must be considered in both sections, since the difficult solubility of its chloride may lead to confounding its oxide with protoxide of mercury and oxide of silver, without affording us, on the other hand, any means of effecting its perfect separation from the oxides of the second section.

§ 91.

FIRST SECTION OF THE FIFTH GROUP : OXIDES PRECIPITABLE BY HYDROCHLORIC ACID.

Special Reactions.

a. OXIDE OF SILVER.   (Ag O).

1. Oxide of siver is a grey brown powder which dissolves readily in dilute nitric acid.   It forms no hydrate.

2. The salts of oxide of silver are non-volatile and colorless; most of them acqui⬤ black tint when exposed to light.   The soluble neutral salts do not alter vegetable colors, and are decomposed at a red heat.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* precipitate black SULPHURET OF SILVER, (Ag S), which is insouble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium.   Boiling concentrated nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

4. *Potassa and ammonia* precipitate from solution of salts of silver, the oxide of this metal in the form of a LIGHT BROWN POWDER, which is insoluble in potassa, but dissolves readily in am-

monia. The presence of salts of ammonia prevents this precipitation totally or partly.

5. *Hydrochloric acid* and *soluble metallic chlorides* produce in solutions of salts of silver a white curdy precipitate of CHLORIDE OF SILVER. (Ag Cl). In very dilute solutions, these reagents impart simply a bluish-white opalescent appearance to the fluid. Chloride of silver, when exposed to the light, acquires first a violet tint, and then turns black; it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-chloride of silver, from which double compound the chloride of silver is separated again by acids. Chloride of silver, when heated, fuses without decomposition, into a transparent horny mass.

6. When compounds of silver, mixed with *carbonate of soda*, are exposed on a charcoal support to the *inner* flame of the blow-pipe, WHITE BRILLIANT AND DUCTILE METALLIC GLOBULES are produced unattended with any incrustation of the charcoal.

b. PROTOXIDE OF MERCURY. (Hg₂ O).

1. Protoxide of mercury is a black powder which is readily soluble in nitric acid, and is decomposed by the action of heat, the mercury volatilizing in the metallic state. It forms no hydrate.

2. The salts of protoxide of mercury, when ignited, volatilize either unaltered, or they are decomposed, and the mercury volatilizes in the metallic state. Most of the protosalts of mercury are colorless. The soluble salts redden litmus paper in the neutral state; when mixed with much water, they decompose into insoluble basic and soluble acid salts.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce black precipitates of PROTOSULPHURET OF MERCURY, (Hg₂ S), which are insoluble, both in dilute acids, in hydrosulphuret of ammonia, and cyanide of potassium. Sulphuret of potassium converts this sulphuret into bisulphuret which dissolves, and globules of metallic mercury, which separate. Protosulphuret of mercury is readily decomposed and dissolved by aqua regia, but not by boiling concentrated nitric acid.

4. *Potassa* and *ammonia* produce in the solution of protosalts of mercury black precipitates, which are insoluble in an excess of the

precipitants. The potassa precipitates consist of PROTOXIDE OF MERCURY; whilst those produced by ammonia consist of a BASIC DOUBLE SALT OF PROTOXIDE OF MERCURY AND AMMONIA, e. g. (N H$_4$ O, N O$_s$ + 3 Hg$_s$ O).

5. *Hydrochloric acid* and *soluble metallic chlorides* precipitate PROTOCHLORIDE OF MERCURY (Hg$_s$ Cl) as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid fail to dissolve this precipitate; it dissolves, however, although very difficultly and slowly, upon long protracted boiling with these acids, being resolved by hydrochloric acid into perchloride of mercury, and metallic mercury which separates, and converted by nitric acid into perchloride of mercury and pernitrate of mercury. Aqua regia and chlorine water dissolves the protochloride of mercury readily, forming perchloride. Ammonia and potassa decompose the protochloride of mercury and separate black protoxide from it.

6. If a drop of neutral or feebly acid solution of protoxide of mercury be poured on a *clean and smooth surface of copper*, and washed off after some time, the spot will subsequently, when rubbed with cloth, paper, &c., appear WHITE and LUSTROUS like silver. The application of heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and removes the silvering.

7. *Protochloride of tin* produces in solutions of protoxide of mercury, a grey precipitate of METALLIC MERCURY, which may be united into globules by heating and agitation, but most readily by boiling with hydrochloric acid.

8. If an intimate mixture of any of the compounds of mercury, with anhydrous *carbonate of soda* be introduced into a drawn-out glass tube, and covered with a layer of carbonate of soda, and the tube be then heated before the blow-pipe, the mercurial compound will undergo decomposition, and metallic mercury will separate, forming a crust of grey sublimate above the heated part of the tube. The minute particles of mercury may be united into globules by rubbing this crust with a glass rod.

c OXIDE OF LEAD.   (Pb O).

1. Oxide of lead is a yellow or reddish-yellow powder which fuses to a vitreous mass when heated.   Hydrated oxide of lead is white.   Both the oxide of lead and its hydrate dissolves in nitric acid and acetic acid.

2. The salts of oxide of lead are colorless and non-volatile; the soluble salts, in the neutral state, redden litmus paper, and are decomposed at a red heat.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce black precipitates of SULPHURET OF LEAD (Pb S), which are insoluble in cold dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium. Sulphuret of lead is decomposed by boiling concentrated nitric acid; the whole of the lead is converted, at first, into nitrate of lead, and the greater portion of the sulphur separates, whilst another portion is converted into sulphuric acid. The sulphuric acid thus formed decomposes a portion of the nitrate of lead, and forms sulphate of lead, which remains un-dissolved in the form of a white powder, mixed with the separated sulphur.—In solutions of salts of lead containing an excess of a mineral acid, sulphuretted hydrogen produces a precipitate only after the addition of water.   When sulphuretted hydrogen is used to throw down lead from the solution containing much free, hydrochloric acid, a reddish precipitate is formed, consisting of chloride and sulphuret of lead, with excess of sulphuretted hydrogen, this is, however, converted into black sulphuret of lead.

4. *Potassa* and *ammonia* throw down BASIC SALT OF LEAD in the form of white precipitates, which are insoluble in ammonia, and of difficult solution in potassa.   Ammonia fails to produce a precipitate in solutions of acetate of lead, owing to the formation of a soluble tri-acetate of lead.

5. *Carbonate of potassa* throws down from solutions of salts of the oxide of lead, a white precipitate of CARBONATE OF LEAD (Pb O, C O$_2$), which is insoluble in an excess of the precipitant and also in cyanide of potassium.

6. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions of salts of the oxide of lead heavy white pre-

cipitates of CHLORIDE OF LEAD, (Pb Cl), which are soluble in a large amount of water, especially upon the application of heat. This chloride of lead is not altered by ammonia, and is more difficult of solution in dilute hydrochloric and nitric acids than in water.

7. *Sulphuric acid* and *sulphates* produces white precipitates of SULPHATE OF LEAD (Pb O, SO₃), which are nearly insoluble in water and dilute acids. From dilute solutions, and especially from those which contain much free acid, the sulphate of lead precipitates only after some time. It is advisible under all circumstances, to add a considerable *excess* of dilute sulphuric acid, since sulphate of lead is far more insoluble in this menstruum than in water. Sulphate of lead is slightly soluble in concentrated nitric acid; it dissolves, with difficulty, in boiling concentrated hydrochloric acid, but more readily in solution of potassa.

8. *Chromate of potassa* produces a yellow precipitate of CHROMATE OF LEAD, (Pb O, Cr O₃), which is readily soluble in potassa, but insoluble in dilute nitric acid.

9. When a mixture of any of the compounds of lead with *carbonate of soda*, is exposed on a charcoal support, to the *reducing flame of the blow-pipe*, soft and ductile METALLIC GLOBULES OF LEAD are readily produced, the charcoal becoming covered, at the same time, with a slight yellow incrustation of OXIDE OF LEAD.

Recapitulation and Remarks.—The metallic oxides of the first section of the fifth group are most distinctly characterized in their corresponding chlorides, since the different deportment of these chlorides with ammonia affords us a simple means both of detecting and of separating them from one another. For the chloride of silver, as I have stated, is dissolved by ammonia, whilst protochloride of mercury and chloride of lead remain undissolved. From the solution of ammonio-chloride of silver which is obtained by treating chloride of silver with ammonia, the simple chloride of silver may be re-precipitated by nitric acid; this reaction admits of no mistake and we require, therefore, no other means to effect the

positive detection of silver. Of the two remaining chlorides, the
protochloride of mercury is converted by ammonia into black pro-
toxide of mercury, whilst the chloride of lead remains unaltered.
The newly-formed protoxide of mercury may be separated from the
chloride of lead by treating the mixed substances with nitric acid,
which dissolves the protoxide of mercury, or by boiling with water,
which effects the solution of the chloride of lead. The protoxide
of mercury is sufficiently characterized by the deportment of the
corresponding chloride with ammonia. Sulphuric acid and chro-
mate of potassa are the most positive tests for the oxide of lead.

§ 92.

SECOND SECTION OF THE FIFTH GROUP.   OXIDES WHICH ARE
NOT PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

a. PEROXIDE OF MERCURY. (Hg O).

1. Peroxide of mercury forms a crystalline mass of a light red
color, inclining sometimes to orange, which upon levigation yields
a powder of a yellowish red color. When heated it acquires a
deeper tint; at a faint red heat, it is resolved into metallic mer-
cury and oxygen. The hydrate of peroxide of mercury is yellow.
Both the peroxide of mercury and its hydrate dissolve readily in
hydrochloric acid, and in nitric acid.

2. The salts of peroxide of mercury volatilize upon ignition;
part of them suffer decomposition in this process, whilst others
remain unaltered. Most of the persalts of mercury are colorless.
The soluble salts in their neutral state redden litmus paper. The
nitrate and sulphate of peroxide of mercury are decomposed into
soluble acid and insoluble basic salts, when treated with a large
amount of water.

3. When a very small amount of *sulphuretted hydrogen* or of
hydrosulphuret of ammonia is added to solutions of persalts of
mercury, and the mixture is agitated, a perfectly white precipitate

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is produced. The addition of somewhat large quantities of these reagents causes the precipitate to acquire a yellow, orange, or brown-red color, according to the less or greater proportion added; an excess of the reagent produces a purely black precipitate of PERSULPHURET OF MERCURY, (Hg S). This progressive variation of color from white to black, which depends on the gradually increasing proportions of the sulphuretted hydrogen, or hydrosulphuret of ammonia, distinguishes the peroxide of mercury from all other substances. The white precipitate which forms at first, consists of a double compound of persulphuret of mercury with the still undecomposed portion of the persalt of mercury (e. g. in a solution of perchloride of mercury, (Hg Cl + 2 Hg S); the gradually increasing admixture of black persulphuret causes the precipitate to pass through the various gradations of color which I have mentioned. Persulphuret of mercury is not dissolved by hydrosulphuret of ammonia, nor by potassa or cyanide of potassium; it is altogether insoluble in hydrochloric acid, and in nitric acid, even upon boiling. It dissolves completely in sulphuret of potassium, and is readily decomposed and dissolved by aqua regia.

4. *Potassa,* when added in a small proportion to neutral or feebly acid solutions of peroxide of mercury, produces a reddish brown precipitate, which acquires a yellow tint when the reagent is added in excess. The *reddish brown* precipitate is a BASIC SALT; the *yellow,* on the contrary, consists of HYDRATED PEROXIDE OF MERCURY. (Hg O, 3 H O). An excess of the precipitant does not re-dissolve these precipitates. In very acid solutions this reaction either does not take place at all, or is at least but incomplete. In presence of salts of ammonia, potassa produces in solutions of persalts of mercury, *white* precipitates, consisting of double compounds of the persalts of mercury with amide of mercury. Thus, for instance, from a solution of perchloride of mercury containing ammoniacal salts in admixture, potassa throws down a double compound of perchloride of mercury with amide of mercury, (Hg Cl + Hg N H$_2$).

5. *Ammonia* produces in solutions of persalts of mercury the

same WHITE PRECIPITATE which potassa produces, when salts of
ammonia are present.

6. *Protochloride of tin*, when added in small portions to salts
of peroxide of mercury, reduces the peroxide to protoxide, giving
rise to the formation of a white precipitate of PROTOCHLORIDE
OF MERCURY, (Hg_2 Cl); but when added in excess, this re-
agent deprives the mercury of the whole of its oxygen and acid
or of the whole of the salt-radical, and therefore throws the
mercury down in the metallic state, just as is the case with pro-
toxide of mercury, (vide § 91, *b.* 7). The precipitate, therefore,
which in the first place was white, acquires now a grey tint, and
may be readily united into globules of metallic mercury, by
boiling with hydrochloric acid.

7. The persalts of mercury present the same deportment as
the protosalts, both with metallic *copper;* and when heated,
in admixture with *carbonate of soda,* in a glass tube before the
blow-pipe.

b. OXIDE OF COPPER. (Cu O).

1. Oxide of copper is a black, fixed powder; its hydrate is of a
light blue color. Both the oxide of copper and its hydrate dis-
solve readily in hydrochloric acid, sulphuric acid, and nitric acid.

2. Most of the neutral salts of oxide of copper are soluble in
water; the soluble salts redden litmus, and suffer decomposition
when heated to gentle redness, with the exception of the sulphate,
which can bear a somewhat higher temperature. They are white
in the anhydrous state; the hydrated salts are of blue or green
color, which their solutions continue to exhibit, even though
much diluted.

3. *Sulphuretted hydrogen* and *hydrosulphuret* of ammonia
produce, in alkaline, neutral, and acid solutions of salts of copper,
blackish brown precipitates of PERSULPHURET OF COPPER (Cu S).
This sulphuret is insoluble in dilute acids and caustic alkalies,
and equally so in hot solutions of sulphuret of potassium and of
sulphuret of sodium; but it is not altogether insoluble in hydro-
sulphuret of ammonia; the latter reagent is, therefore, not adapted
to effect the perfect separation of persulphuret of copper from

other metallic sulphurets. Persulphuret of copper is readily de-
composed and dissolved by boiling concentrated nitric acid; it
dissolves, also, completely in solution of cyanide of potassium. In
solutions of salts of copper which contain an excess of a concen-
trated mineral acid, sulphuretted hydrogen produces a precipitate
only after the addition of water.

4. *Potassa* produces a light blue, bulky precipitate of HYDRATED
OXIDE OF COPPER, (Cu O, HO). If the solution be highly con-
centrated, and the potassa be added in excess, the precipitate will,
after the lapse of some time, turn black, and lose its bulkiness,
even in the cold; but, at all events, upon boiling with the fluid
in which it is suspended, and which, if necessary, is to be diluted
for this purpose. In this process the hydrated oxide is converted
into simple oxide.

5. *Carbonate of potassa* produces, in solutions of salts of
copper, a greenish-blue precipitate of HYDRATED BASIC CARBONATE
OF COPPER, (Cu O, C O$_2$, + Cu O, HO), which, upon boiling,
changes to dark brown oxide of copper, and dissolves in am-
monia to an azure blue, and in cyanide of potassium, to a
brown fluid.

6. *Ammonia,* when added in a small portion to solutions of
salts of copper, produces a GREENISH BLUE precipitate, consisting
of a BASIC SALT OF COPPER. This precipitate redissolves readily
in an excess of the precipitant, yielding a perfectly clear solution
of a magnificent azure blue, which owes its color to the formation
of a BASIC DOUBLE SALT OF AMMONIO-OXIDE OF COPPER. Thus,
for instance, in a solution of sulphate of copper, ammonia pro-
duces a precipitate of (N H$_3$, Cu O + N H$_4$ O, S O$_3$). The blue
color of the fluid is still perceptible unless the solution be very
considerably diluted. Potassa produces in such blue solutions
in the cold, after the lapse of some time, a precipitate of hy-
drated oxide of copper, but, upon boiling, this reagent preci-
pitates the whole of the copper as black oxide. Carbonate of
ammonia presents the same deportment with salts of copper, as
pure ammonia.

7. *Ferrocyanide of potassium* produces even in highly dilute

solutions, a ruddy-brown precipitate of FERROCYANIDE OF COPPER (Cfy, 2 Cu) which is insoluble in dilute acids, but suffers decomposition when acted upon by potassa.

8. *Metallic iron*, when brought into contact with concentrated solutions of salts of copper, is almost immediately covered with a RED CRUST OF METALLIC COPPER; highly dilute solutions produce this coating only after the lapse of some time. This test is extremely delicate ; the reaction is most speedy when the solution contains a free acid, (hydrochloric acid).

9. When a mixture of any of the compounds of copper with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blow-pipe*, METALLIC COPPER is obtained without simultaneous incrustation of the charcoal. The best method of freeing this copper from the surrounding particles of charcoal, is to triturate the whole mass in a small mortar with some water, and to wash off the charcoal powder. The metallic spangles of copper will remain.

c. OXIDE OF BISMUTH. (Bi O_3).

1. Oxide of bismuth is a yellow powder which acquires a deeper tint when heated; it fuses at a red-heat. Hydrated oxide of bismuth is white. Both the oxide of bismuth and its hydrate dissolve readily in hydrochloric acid, sulphuric acid, and nitric acid.

2. The salts of bismuth are non-volatile, with the exception of a few, (chloride of bismuth). Most of them are decomposed at a red-heat. They are colorless ; some of them are soluble in water, whilst others are insoluble in this menstruum. The soluble salts, in the neutral state, redden litmus paper, and are decomposed into soluble acid and insoluble basic salts when treated with a large amount of water.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce, in neutral and acid solutions of salts of bismuth, black precipitates of SULPHURET OF BISMUTH (Bi S_3) which are insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide

of potassium, but are readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of bismuth which contain an excess of concentrated hydrochloric or nitric acid, sulphuretted hydrogen produces a precipitate only after the addition of water.

4. *Potassa* and *ammonia* throw down from solutions of salts of bismuth, HYDRATED OXIDE OF BISMUTH as a white precipitate, which is insoluble in an excess of the precipitants.

5. *Carbonate of potassa* throws down from solutions of salts of bismuth, BASIC CARBONATE OF BISMUTH ($\dot{B}i \ O_3$, CO_2) as a white bulky precipitate, which is insoluble in an excess of the precipitant, and equally so in cyanide of potassium.

6. *Chromate of potassa* precipitates from solutions of salts of bismuth CHROMATE OF BISMUTH as a yellow powder. This substance differs from chromate of lead, inasmuch as it is soluble in dilute nitric acid, and insoluble in potassa.

7. The reaction which characterizes the oxide of bismuth, more particularly, is the decomposition of its neutral salts by *water* into acid soluble and basic insoluble salts. The addition of a large amount of water to solutions of salts of bismuth causes the immediate formation of a dazzling white precipitate, provided there be not too much free acid present. This reaction is the most susceptible in the case of chloride of bismuth, since the basic chloride of bismuth ($Bi \ Cl_3$, $2 \ Bi \ O_3$) is nearly insoluble in water. Should water fail to produce a precipitate in nitric solutions of bismuth, owing to the presence of too much free acid, a precipitate will immediately form, upon neutralizing the free acid with an excess of basic acetate of lead; we must, of course, be fully convinced of the absence of sulphuric acid, &c., before we can have recourse to the application of this means. From the basic salts of antimony which are formed under analogous circumstances, the precipitated basic salts of bismuth may be readily distinguished by their insolubility in tartaric acid.

8. When a mixture of any of the compounds of bismuth, with *carbonate of soda*, is exposed on a charcoal support, to the *reducing flame of the blow-pipe*, BRITTLE GRAINS OF BISMUTH are ob-

tained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered, at the same time, with a slight yellow incrustation of OXIDE OF BISMUTH.

d. OXIDE OF CADMIUM. (Cd O).

1. Oxide of cadmium is a yellowish brown, fixed powder. The hydrated oxide is white. Both the oxide of cadmium and its hydrate dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid.

2. The salts of oxide of cadmium are either colorless or white ; most of them are soluble in water. The soluble salts, in the neutral state, redden litmus paper, and are decomposed at a red-heat.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce, in alkaline, neutral, and acid solutions of salts of cadmium, a bright yellow precipitate of SULPHURET OF CADMIUM, (Cd S), which is insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium, but is readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of cadmium which contain a considerable excess of free acid, sulphuretted hydrogen produces a precipitate only after the addition of water.

4. *Potassa* produces, in solutions of salts of cadmium, a white precipitate of HYDRATED OXIDE OF CADMIUM (Cd O, H O) which is insoluble in an excess of the precipitant.

5. *Ammonia* likewise precipitates from solutions of salts of cadmium white HYDRATED OXIDE OF CADMIUM, but this redissolves readily to a colorless fluid, upon addition of ammonia in excess.

6. *Carbonate of potassa* and *carbonate of ammonia* produce white precipitate of CARBONATE OF CADMIUM (Cd O, C O$_2$) which are insoluble in an excess of the precipitants. The presence of salts of ammonia does not prevent the formation of these precipitates. The precipitated carbonate of cadmium dissolves readily in solution of cyanide of potassium.

7. When a mixture of any of the compounds of cadmium with *carbonate of soda* is exposed on a charcoal support, to the *reducing flame of the blow-pipe*, the charcoal becomes covered

with a reddish yellow incrustation of OXIDE OF CADMIUM, owing to the volatilization of the reduced metal and its subsequent reoxidation in passing through the oxidizing flame.

Recapitulation and remarks.—The perfect separation of the metallic oxides of the second section of the fifth group, from protoxide of mercury and oxide of silver, may, as I have already stated, be effected by means of hydrochloric acid ; but this agent fails to separate them completely from oxide of lead. The peroxide of mercury differs from the other oxides of this section, inasmuch as the corresponding sulphuret is insoluble in boiling nitric acid. This property affords a convenient means for its separation. Moreover, the reactions with protoxide of tin, or with metallic copper, as well as those in the dry way, will readily indicate the presence of peroxide of mercury, after the previous removal of the protoxide.

The oxides of copper and cadmium differ from those of lead and bismuth, inasmuch as the precipitates which ammonia causes in solutions of the salts of the former, are soluble in an excess of ammonia, whilst the precipitates which this reagent produces in solutions of the salts of the latter do not redissolve in an excess of the precipitant. The oxide of bismuth may be separated from the oxide of lead by means of sulphuric acid; but the most characteristic reaction of the oxide of bismuth is, as I have already stated, the decomposition of its salts by water. For the most certain detection of lead, I refer to § 91, *c.* 7 and 8. The oxide of copper may be separated from the oxide of cadmium, by means of carbonate of ammonia; the former is more particularly characterized by the reactions with ferrocyanide of potassium and with iron, and also by the deportment of its salts before the blow-pipe, whilst the oxide of cadmium may invariably be detected by its yellow sulphuret, which is insoluble in hydrosulphuret of ammonia, and by the characteristic incrustation with which its salt covers the charcoal support when exposed to the reducing flame of the blow-pipe. For the method of separating the oxides of the fifth group from one another by

means of cyanide of potassium, I refer to the second section of Part II. (Additional remarks to § 120).

§ 93.

Sixth Group.

PEROXIDE OF GOLD—PEROXIDE OF PLATINUM—OXIDE OF ANTI-MONY—PEROXIDE OF TIN—PROTOXIDE OF TIN—ARSENIOUS AND ARSENIC ACID. *

Properties of the group.—The sulphurets corresponding with the oxides of the sixth group are insoluble in dilute acids.   These oxides combine with alkaline sulphurets, forming soluble sulphur salts, in which they perform the part of the acid.   Sulphuretted hydrogen, consequently precipitates these oxides completely from acidified but not from alkaline solutions.   The precipitated sulphurets dissolve in hydrosulphuret of ammonia, sulphuret of potassium, &c., and re-precipitate from these solutions upon the addition of acids.

We divide the oxides of this group into two classes, and distinguish,

1. OXIDES, OF WHICH THE CORRESPONDING SULPHURETS ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, viz. peroxide of gold and peroxide of platinum.

2. OXIDES, OF WHICH THE CORRESPONDING SULPHURETS ARE SOLUBLE IN HYDROCHLORIC ACID OR NITRIC ACID, viz.: oxide of antimony, protoxide and peroxide of tin, arsenious and arsenic acids.

§ 94.

First Class.

Special Reactions.

a. PEROXIDE OF GOLD.   (Au O_3).

1. Peroxide of gold is a blackish brown powder ; its hydrate is

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* I have placed the two acids of arsenic with the metallic oxides, since the deportment of sulphuret of arsenic may readily lead to their being confounded with some of the oxides of the sixth group, and because in the systematic course of analysis the sulphuret of arsenic is invariably precipitated with sulphuret of antimony, sulphuret of tin, &c. &c.

chestnut brown. Both the peroxide of gold and its hydrate are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve peroxide of gold ; water re-precipitates it from these solutions.

2. Salts of gold with oxygen acids are nearly unknown. The haloid salts of gold are yellow, and their solutions continue to exhibit this color up to a high degree of dilution. The whole of them are readily decomposed upon ignition ; the soluble salts, in the neutral state, redden litmus paper.

3. *Sulphuretted hydrogen* precipitates from neutral and acid solutions of salts of gold, the whole of the metal as black PER-SULPHURET OF GOLD (Au S_3) which is insoluble in simple acids, partly soluble in potassa, and perfectly so in sulphuretted alkaline sulphurets and in aqua regia. It is, however, insoluble when boiled with ammonia and free sulphur.

4. *Hydrosulphuret of ammonia* produces the same precipitate, which redissolves in an excess of the precipitant only if the latter contains an excess of sulphur.

5. *Potassa* produces in tolerably concentrated solutions of salts of gold a reddish yellow precipitate of PEROXIDE OF GOLD, which acquires a deeper color upon boiling ; the precipitate is insoluble in an excess of potassa, and invariably contains salts of gold, and also potassa in admixture. Potassa fails to precipitate acid solutions of salts of gold in the cold.

6. *Ammonia* produces only in tolerably concentrated solutions of salts of gold, reddish yellow precipitates of AURATE OF AMMONIA (fulminating gold). In solutions which contain free acid or ammoniacal salts, this precipitate forms only upon boiling.

7. *Protochloride of tin*, containing an admixture of perchloride, produces even in extremely dilute solutions of gold, a purple-red precipitate, (or coloration at least,) which sometimes inclines rather to violet or to brown-red. This precipitate, which has received the name of PURPLE OF CASSIUS, is insoluble in hydrochloric acid. It is represented to be a hydrated compound of oxide of tin, and protoxide of gold with sesquioxide of tin (Au O, Sn O_2 + Sn_2 O_3 + 4 H O).

8. *Protosalts of iron* reduce the peroxide of gold when added to its solutions, and precipitate metallic gold in the form of a very fine brown powder, which acquires metallic lustre, when pressed upon with the blade of a knife, or when rubbed. The fluid in which the precipitate is suspended, appears of a blackish-blue color, by transmitted light.

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b. PEROXIDE OF PLATINUM. (Pt O_4).

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1. Peroxide of platinum is a blackish-brown, its hydrate a reddish-brown powder. The peroxide of platinum and its hydrate are reduced by heat; they are both readily soluble in hydrochloric acid, and difficultly soluble in oxygen acids.

2. The persalts of platinum are decomposed at a red-heat. They are of a reddish-brown color, which their solutions continue to exhibit even though considerably diluted. The soluble salts in the neutral state redden litmus paper.

3. *Sulphuretted hydrogen* throws down from acid and neutral solutions—(but not from alkaline solutions, at all events, not completely)—after the lapse of some time, a blackish-brown precipitate of BISULPHURET OF PLATINUM (Pt S_2). If the solution is heated, after the addition of the sulphuretted hydrogen, this precipitate forms *immediately*. It is soluble in a considerable excess of potassa or of alkaline sulphurets, and more particularly of those containing an excess of sulphur. Bisulphuret of platinum is insoluble in hydrochloric acid and in nitric acid, but it dissolves readily in aqua regia. When boiled with ammonia and free sulphur it will not dissolve.

4. *Hydrosulphuret of ammonia* produces the same precipitate, this redissolves completely in a large excess of the precipitant, if the latter contains an excess of sulphur. Acids reprecipitate the bisulphuret of platinum unaltered from this solution.

5. *Potassa and ammonia* produce in solutions of salts of platinum, when not too highly dilute, yellow crystalline precipitates of POTASSIO-CHLORIDE OF PLATINUM, and AMMONIO-CHLORIDE OF PLATINUM, which are insoluble in acids, but dissolve in an excess of the precipitants, upon the application of heat. The presence of a little free hydrochloric acid promotes the precipitation

greatly, since the acid effects the conversion of the free alkalies into chlorides.

6. *Protochloride of tin* does not produce a precipitate in solutions of persalts of platinum which contain much free hydrochloric acid, it simply imparts to them an INTENSELY DEEP BROWNISH-RED COLOR, owing to a reduction of the peroxide or bichloride of platinum, to protoxide or simple chloride.

Recapitulation and Remarks.—The reactions of gold and platinum, or at least some of them, are sufficiently characteristic for the detection of these two metals, even though many other oxides be present. Protochloride of tin and protoxide of iron are the most characteristic reagents for gold; potassa and ammonia in presence of free hydrochloric acid, or, what comes to the same point, chloride of potassium and chloride of ammonium, are the most positive tests for platinum.

§ 95.

Second Section of the Sixth Group.

Special Reactions.

a. OXIDE OF ANTIMONY. (Sb O_3).

1. The oxide of antimony presents, according to the mode of its preparation, either white, brilliant, crystalline needles, or a greyish white powder. It fuses at a gentle red heat, and when exposed to a higher temperature, volatilizes unaltered. It is insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acids. Oxide of antimony is easily reduced to the metallic state by fusion with cyanide of potassium.

2. Part of the salts of oxide of antimony are decomposed upon ignition; the haloid salts volatilize readily, and unaltered. The soluble neutral salts of antimony redden litmus paper. When treated with a large amount of water, they are resolved into insoluble basic, and soluble acid salts. Thus, for instance, water throws down from solutions of protochloride of antimony in hydrochloric acid, a white bulky precipitate of basic chloride of antimony (powder of Algaroth) Sb Cl_3, 5 Sb O_3, which after

some time becomes heavy and crystalline. Tartaric acid dissolves
this precipitate readily, and of course prevents its formation if
mixed with the solution previously to the addition of the water.
It is by this property that the basic protochloride of antimony is
distinguished from the basic salts of bismuth formed under similar
circumstances.

3. *Sulphuretted hydrogen* precipitates from acid solutions of
oxide of antimony, the whole of this metal, as orange-red PROTO-
SULPHURET OF ANTIMONY (Sb S_3). In alkaline solutions, this
reagent fails to produce a precipitate, or, at least, to throw down the
whole of the antimony present; neutral solutions also are but
imperfectly precipitated by sulphuretted hydrogen. The protosul-
phuret of antimony thus produced is readily dissolved by potassa
and by alkaline sulphurets, especially if the latter contain an ex-
cess of sulphur, whilst it is but sparingly soluble in ammonia, and
almost insoluble in bicarbonate of ammonia, that is, if the precipi-
tate is free from any admixture of sulphur, and also of sulph-
antimonious and sulphantimonic acids. It is insoluble in dilute
acids. Concentrated boiling hydrochloric acid dissolves it, with
evolution of sulphuretted hydrogen gas. When heated in the air,
it is converted into a mixture of antimonious acid and proto-
sulphuret of antimony. When deflagrated with nitrate of soda, it
yields sulphate of soda and antimoniate of soda. If a potassa
solution of protosulphuret of antimony be boiled with oxide of
copper, sulphuret of copper will precipitate, and oxide of anti-
mony dissolved in potassa will remain in solution. On fusing
sulphuret of antimony with cyanide of potassium, metallic anti-
mony and sulphocyanide of potassium will be produced. If the
operation be conducted in a small tube expanded into a bulb at
the lower end, or in a stream of carbonic acid gas (vide § 95, *d.*
10) no sublimate of antimony will be produced. But if a mixture
of sulphuret of antimony with carbonate of soda, or of cyanide of
potassium and carbonate of soda, be heated in a glass tube, in a
stream of hydrogen, (compare § 95, *d.* 3,) a mirror of antimony
will be deposited on the inner surface of the tube, immediately
behind the spot occupied by the mixture.

4. *Hydrosulphuret of ammonia* produces an orange-red pre-

cipitate of PROTOSULPHURET OF ANTIMONY, which readily redissolves in an excess of the precipitant, if the latter contains an excess of sulphur ; it also dissolves when boiled with ammonia and
free sulphur : from these solutions acids precipitate the pentasulphuret of antimony (Sb S_5), which, under these circumstances,
however, assumes a yellow color from the sulphur thrown down
with it.

5. *Potassa, ammonia, carbonate of potassa,* and *carbonate of
ammonia,* throw down from solutions of protochloride of antimony, also from solutions of simple salts of antimony,—but not,
or at least not immediately, from solutions of tartar emetic or
analogous compounds,—a white and bulky precipitate of OXIDE
OF ANTIMONY, which redissolves readily in an excess of potassa,
but requires the application of heat for its re-solution in carbonate
of potassa or carbonate of ammonia, and is altogether insoluble in
an excess of ammonia.

6. *Metallic zinc* precipitates from all solutions of oxides of
antimony, unless free nitric acid be present, METALLIC ANTIMONY
as a black powder.   Should the solution under examination contain free nitric acid, oxide of antimony will precipitate with the
metal.

7. When a solution of oxide of antimony is brought into contact with *zinc* and *sulphuric acid,* the zinc oxidizes not only at
the expense of the oxygen of the water, but also at the expense of
that of the oxide of antimony, and the antimony separates in a
metallic state ; but a portion of the metal combines in the moment
of its separation with the liberated hydrogen of the water forming.
ANTIMONIURETTED HYDROGEN (Sb H_3).   If this operation be
conducted in a gas-evolution flask, connected by means of a perforated cork with the limb of a bent tube, of which the other limb
ends in a finely drawn-out point, pinched off at the top,* and the
hydrogen passing through the fine aperture of the tube, be kindled, after all atmospheric air has been previously expelled, the

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* In accurate and precise experiments it is necessary to transmit the gas
first through another tube, loosely filled with cotton, to prevent any moisture
being carried into the exit tube.   Compare the engraving of Marsh's apparatus, § 95, *d.* 8.

flame will appear of a bluish-green tint, which is imparted to it by the antimony separating in a state of intense ignition upon the combustion of the antimoniuretted hydrogen ; white fumes of oxide of antimony rise from the flame, which condense readily upon cold substances, and are not dissolved by water. If a cold substance (such as a porcelain plate) be now depressed upon the flame, METALLIC ANTIMONY will be deposited upon the surface of the plate, in a state of the most minute division, forming a deep black and almost lustreless spot. If the tube through which the gas is passing be heated to redness, in the centre, the bluish-green tint of the flame will decrease in intensity, and a metallic mirror of antimony of silvery lustre will form within the tube on both sides of the ignited part. If dry sulphuretted hydrogen be now very slowly transmitted through this tube, and the mirror be heated by means of a spirit-lamp, proceeding from its outer towards its inner extremity, that is, in an opposite direction to that of the gas, the mirror of the antimony will become converted into sulphuret of antimony, which appears of a more or less reddish-yellow color, and almost black when in thick layers. If a feeble stream of hydrochloric acid gas be transmitted through the same glass tube, the sulphuret of antimony, when present in thin layers only, will disappear immediately, and, after a few seconds, when the incrustation is somewhat thicker. The reason for this is, that the sulphuret of antimony decomposes readily with hydrochloric acid, and the protochloride of antimony formed is exceedingly volatile in hydrochloric acid gas. If this gas be now transmitted through water, the presence of antimony in the latter may readily be proved by means of sulphuretted hydrogen. By this combination of reactions, antimony may be distinguished with positive certainty from all other metals.

8. If compounds of antimony, mixed with *carbonate of soda and cyanide of potassium* be exposed on a charcoal support, to the *reducing flame of the blow-pipe*, brittle globules of ME-TALLIC ANTIMONY will be produced, attended with volatilization of the reduced and reoxidized metal, which continues for some time after its removal from the flame, and is more particularly manifest when a stream of air is directed, by means

of the blow-pipe, upon the surface of the cooling mass. The oxide of antimony formed is partly deposited on the charcoal as a white crust, and partly surrounds the metallic globules in the form of fine crystalline needles.

b. PROTOXIDE OF TIN. (Sn O).

1. Protoxide of tin is a black or greyish-black powder; its hydrate is white. Protoxide of tin is readily reduced by fusion with cyanide of potassium. It is readily soluble in hydrochloric acid. Nitric acid converts it into peroxide of tin, which is insoluble in an excess of the acid.

2. The protosalts of tin are colorless, and are decomposed by heat. The soluble salts in the neutral state redden litmus paper. The addition of water to solutions of neutral protosalts of tin produces a milkiness in them; this is owing to the decomposition of the neutral salt into a soluble acid, and an insoluble basic salt; the solution again clears upon addition of hydrochloric acid.

3. *Sulphuretted hydrogen* throws down from neutral and acid solutions of protosalts of tin a dark brown precipitate of HYDRATED PROTOSULPHURET OF TIN, (Sn S,) which is soluble in potassa and in alkaline sulphurets, especially in sulphuretted alkaline sulphurets, and equally so in concentrated boiling hydrochloric acid. Boiling nitric acid converts it into insoluble peroxide of tin. Alkaline solutions of protosalts of tin are not, or, at any rate but imperfectly, precipitated by sulphuretted hydrogen.

4. *Hydrosulphuret of ammonia* produces the same precipitate of HYDRATED SULPHURET OF TIN. This precipitate redissolves with very great difficulty in an excess of the precipitant; but it is readily soluble in hydrosulphuret of ammonia containing an excess of sulphur, (this may be at once seen by the yellow color of the reagent). Or if boiled with ammonia to which sulphur is added, its solution is instantly effected. From these solutions acids precipitate hydrated yellow bisulphuret of tin (Sn S₂) with sulphur.

5. *Potassa, ammonia, carbonate of potassa,* and *carbonate of*

ammonia, produce a white bulky precipitate of HYDRATED PRO-
TOXIDE OF TIN, (Sn O, H O,) which redissolves readily in an
excess of potassa, but is insoluble in an excess of the other three
precipitants.   Upon heating a concentrated solution of the hy-
drated protoxide of tin in potassa, the protoxide is converted into
peroxide, which remains in solution, and metallic tin, which sepa-
rates in the form of brown flakes.

6. *Perchloride of gold* produces in solutions of protochloride
or protoxide of tin, upon the addition of some nitric acid, (without
application of heat,) a precipitate or coloration of PURPLE OF
CASSIUS, (compare § 94, *a.* 7).

7. Solution of *perchloride of mercury*, when added in excess,
produces in solutions of protochloride or protoxide of tin, a white
precipitate of PROTOCHLORIDE OF MERCURY, owing to the protosalt
of tin withdrawing from the perchloride of mercury one half of its
chlorine.

8. If proto-compounds of tin be mixed with *carbonate of soda*
and some *borax*, or, better still, with equal parts of *carbonate of
soda* and *cyanide of potassium*, and the mixture exposed on a
charcoal support to the *inner blow-pipe flame*, ductile grains of
METALLIC TIN will be obtained, unattended with any incrustation
of the charcoal.   The best way of freeing these grains of metallic
tin from the surrounding particles of charcoal, is to triturate the
whole mass with water, in a small mortar—(in which operation
some force should be used)—and to wash the charcoal off from
the metallic particles.

c. PEROXIDE OF TIN.   (Sn O_2).

1. Peroxide of tin is a white or straw-coloured precipitate,
which by boiling passes into a brown powder.   It forms two series
of salts with acids, bases, and water.   The hydrate precipitated by
alkalies from protosalts dissolves readily in potassa and acids,
whilst that formed by nitric acid does not dissolve ; by drying,
the former is converted into the latter oxide.

2. The persalts of tin are colorless, and are decomposed at a
red-heat.   The soluble persalts of tin in the neutral state redden
litmus paper.

3. *Sulphuretted hydrogen* throws down, from acid and neutral solutions, a yellow precipitate of HYDRATED BISULPHURET OF TIN, (Sn S$_2$). The application of heat promotes its formation. Alkaline solutions are not precipitated by this reagent. The bisulphuret of tin dissolves readily in potassa, alkaline sulphurets, and concentrated boiling hydrochloric acid. It dissolves with difficulty in pure ammonia and in carbonate of ammonia. Nitric acid converts it into insoluble peroxide of tin. Upon deflagrating bisulphuret of tin with nitrate of soda, sulphate of soda and stannate of soda are produced. When a solution of bisulphuret of tin in potassa is boiled with oxide of copper, sulphuret of copper and peroxide of tin are formed, the latter substance remaining dissolved in the potassa solution.

4. *Hydrosulphuret of ammonia* produces a precipitate of HYDRATED BISULPHURET OF TIN, (Sn S$_2$,) which redissolves readily in an excess of the precipitant. From this solution acids reprecipitate the bisulphuret of tin unaltered.

5. *Potassa, ammonia, carbonate of potassa,* and *carbonate of ammonia,* precipitate white HYDRATED PEROXIDE OF TIN, (Sn O$_2$, H O), which dissolves readily in an excess of potassa. It is more sparingly soluble in ammonia, and most so in alkaline carbonates.

6. *Metallic zinc* precipitates from solutions of perchloride or persalts of tin, which contain no free nitric acid, METALLIC TIN in the shape of small grey scales, or as a spongy mass. Should free nitric acid be present in the solution under examination, white HYDRATED PEROXIDE OF TIN will precipitate instead, or a mixture of metallic tin with hydrated peroxide.

7. The compounds of the peroxide of tin manifest the same deportment before the blow-pipe as the proto-compounds.

d. ARSENIOUS ACID. (As O$_3$).

1. Arsenious acid appears generally either as a transparent vitreous, or as a white porcelain-like mass; when levigated, it forms a heavy white powder; when heated, it volatilizes in white inodorous fumes. It is difficultly soluble in cold, but more readily so in hot water. Hydrochloric acid and potassa dissolve it copiously.   K 2

2. The arsenites are decomposed upon ignition mostly into more fixed arseniates, and into metallic arsenic, which volatilizes. None of the arsenites, except those with alkaline bases, are soluble in water. The insoluble arsenites are dissolved, or, at least decomposed by hydrochloric acid.

3. *Sulphuretted hydrogen* precipitates the solutions of arsenious acid and of neutral arsenites, slowly and imperfectly, except a free acid be present, when the precipitation will be immediate and perfect. Alkaline solutions are not precipitated. The precipitates are of a bright yellow color; they consist of SULPHARSENIOUS ACID, (As S_3,) and are readily and completely dissolved by pure alkalies, alkaline carbonates, and bicarbonates, and like-wise by alkaline sulphurets, but are nearly insoluble in hydrochloric acid. Boiling nitric acid decomposes and dissolves sulpharsenious acid readily. The deflagration of sulpharsenious acid with carbonate of soda and nitrate of soda gives rise to the formation of arseniate and sulphate of soda. When a solution of sulpharsenious acid in potassa is boiled with oxide of copper, sulphuret of copper and arseniate of potassa are formed. Upon boiling a similar solution with a hydrated carbonate or basic nitrate of bismuth, sulphuret of bismuth and arsenite of potassa are produced. If a mixture of sulpharsenious acid, with from three to four parts of carbonate of soda, and some water, to form it into a paste, be spread over some small pieces of glass, and well dried, then rapidly heated to redness, in a glass tube, through which dry hydrogen gas is transmitted, the whole of the arsenic present will be reduced to the metallic state, and expelled. Part of the reduced arsenic forms a metallic mirror on the inner surface of the tube, the rest is carried away, suspended in the hydrogen gas; these minute particles of arsenic impart a bluish tint to the hydrogen when kindled, and form stains of arsenic upon the surface of a porcelain plate depressed upon the flame. It is erroneous to suppose that arseniuretted hydrogen is formed in this process, although it might seem to be the case from the circumstance that, upon heating another part of the tube to redness, a fresh metallic mirror will be produced immediately behind the ignited place; but this is simply owing to the suspended particles of arsenic being reconverted into

arsenical fumes, which condense upon the cold part of the tube. That this is in reality the case, may be readily ascertained by conducting the hydrogen gas charged with the particles of arsenic, through water, and afterwards through a long tube, filled with moistened cotton ; if this be done, pure hydrogen gas will escape from the end of the tube, and all the arsenic will be retained by the water and the cotton in the form of a black powder. The fusion of two equivalents of sulpharsenious acid, with four equivalents of soda, gives rise at first to the formation of a double sulphuret of arsenic and sodium, and of arsenite of soda. Upon heating these products in hydrogen gas, at first the arsenious acid alone undergoes reduction ; but upon the application of a more intense heat, the sulpharsenious acid is also reduced to the metallic state. This method of reduction yields indeed very accurate results, but it does not enable us to distinguish arsenic from antimony with a sufficient degree of safety, nor to pronounce positively upon the presence or absence of arsenic in cases where antimony also is present, (compare § 95, *a.* 3).

The operation is to be conducted in the apparatus illustrated by

PLATE IV.
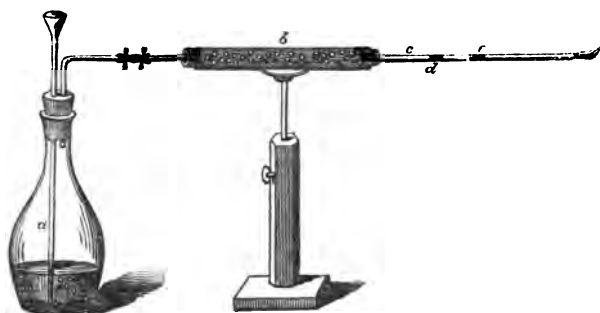
a is the evolution flask, *b* a tube containing chloride of calcium, *c* the tube in which, at the point *d*, the glass splinter with the mixture of sulpharsenious acid and carbonate of soda is placed. As soon as the apparatus is completely filled with pure hydrogen gas, *d* is exposed at first to a gentle heat, in order to expel all

the moisture which may still be present, and then suddenly raised
to a very intense heat, to prevent the sublimation of undecom-
posed sulphuret of arsenic. The metallic mirror is deposited
near the point *e*; the sudden application of a very strong heat is
best effected by means of the blow-pipe. A new method of effect-
ing the reduction of sulphuret of arsenic to the metallic state,
and which combines with the very highest degree of delicacy this
advantage, that it precludes the possibility of confounding arsenic
with antimony, will be found described at § 95, *d.* 10.

4. *Hydrosulphuret of ammonia* produces also a precipitate
of SULPHARSENIOUS ACID. In neutral and alkaline solutions,
however, the sulpharsenious acid, instead of precipitating, remains
dissolved as a double sulphuret of arsenic and ammonium, but it
precipitates from this solution immediately upon the addition of a
free acid.

5. *Nitrate of silver* produces in neutral solutions of the arse-
nites, a yellow precipitate of ARSENITE OF SILVER, $(2 \text{ Ag O},$
$\text{As O}_3)$ which is soluble both in dilute nitric acid and in ammonia.
Ammonio-nitrate of silver produces a similar precipitate in solu-
tions of arsenious acid, or of arsenites, when containing free acid.

6. *Sulphate of copper* and *ammonio-sulphate of copper* pro-
duce, under the same circumstances as the salts of silver, yellow-
green precipitates of ARSENITE OF COPPER, $(2 \text{ Cu O}, \text{ As O}_3)$.

7. If to a solution of arsenious acid in an excess of *caustic
potassa*, or to the solution of an alkaline arsenite, mixed with
caustic potassa, a few drops of a dilute solution of sulphate of
copper be added, and the mixture boiled, a red precipitate of
SUBOXIDE OF COPPER will fall down, and the solution will now
contain arseniate of potassa. This reaction is exceedingly deli-
cate, provided a minute quantity only of solution of sulphate of
copper be used. Even should the red precipitate of suboxide of
copper be so exceedingly minute as to escape detection in trans-
mitted light, yet it will be discernible still with great distinctness
upon looking in at the top of the test tube. Of course this re-
action, although really of great importance in certain instances,
as a confirmatory proof of the presence of arsenious acid, and
more particularly as a means of distinguishing arsenious acid

from arsenic acid, is yet utterly inapplicable for the *direct detection* of arsenic, since grape sugar and other organic substances also separate suboxide of copper from salts of copper in the same manner.

8. If an acid or neutral solution of arsenious acid, or of an arsenite, be mixed with *zinc, water,* and *sulphuric acid,* ARSENIURETTED HYDROGEN (As H_3) will be formed; in the same manner as compounds of antimony, under analogous circumstances yield antimoniuretted hydrogen. Compare § 95, *a.* 7. This deportment of arsenic affords us a most delicate test for the detection of this substance, and likewise a very valuable means to effect its isolation.

The process is invariably conducted in the apparatus illustrated by Plate V., and which has already been alluded to at § 95, *a.* 7. (Oxide of antimony.)

PLATE V.
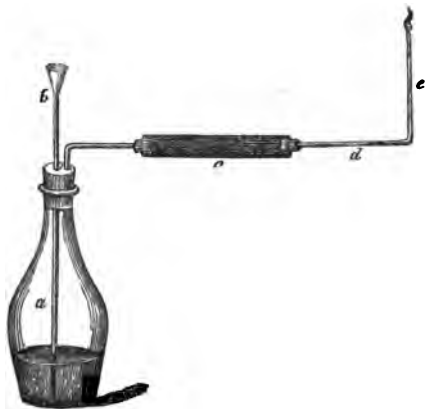
a is the evolution flask, containing water and fragments of metallic zinc; *b* is a funnel-tube, through which the sulphuric acid, and subsequently the fluid to be tested for arsenic, are poured into the flask; *c* is a glass tube, loosely filled with cotton, or, better still, with fragments of fused chloride of calcium, and to which a bent tube (*d e*) of DIFFICULTLY FUSIBLE glass, is fitted by means of a perforated cork; the limb *c* of this tube is drawn

out into a point, and pinched off at the top. When the evolu-
tion of hydrogen has proceeded for a considerable time, so that
it may safely be concluded that all atmospheric air has been
expelled from the apparatus, the gas is kindled at the aperture of
the tube *d e*. (It is advisable to envelope the flask with a piece
of cloth before kindling the gas, as an effectual means of prevent-
ing accidents should an explosion take place.) It is now abso-
lutely necessary to ascertain, first, whether the zinc and the
sulphuric acid are quite free from any admixture of arsenic. This
is effected, 1st, by depressing a porcelain plate upon the
flame; and, 2nd, by heating the central part of the tube *d e* to
redness, for which purpose the limb *e* is to be turned into a hori-
zontal position. If no incrustation appear, either on the plate
or within the tube, this may be considered a proof of the perfect
freedom of the zinc and sulphuric acid from the slightest admixture
of arsenic. The fluid to be tested is then introduced into the
flask through the funnel-tube. Should it contain arsenic, arse-
niuretted hydrogen will be evolved with the hydrogen; and this
arseniuretted hydrogen will impart a bluish tint to the flame,
owing to the separation and ignition of the arsenic. At the-same
time white fumes of arsenious acid arise, which condense upon
cold objects. If a porcelain plate be now depressed upon the flame,
the separated and not yet reoxidized arsenic will condense upon
the plate in the form of black spots. (Vide antimony, § 95, *a.*
7). The spots formed by arsenic are of a rather blackish-brown
color, and bright metallic lustre; whilst those of antimony are of
a deep black color, and but feebly lustrous. If the central part
of the limb *d* be heated to redness, the arsenic will condense in
the cold part of the tube, forming a particularly beautiful and
distinct metallic mirror, which is of darker and less silvery white
hue than that formed by antimony under similar circumstances,
and may be, moreover, distinguished from the latter by the cha-
racteristic odor of garlic, which becomes manifest upon cutting
the tube off close to the mirror, and volatilizing the latter in the
air, by the application of heat. Should the formation of metallic
spots upon the porcelain plate seem to indicate the presence of
arsenic, it will be necessary still to ascertain beyond the possibility

of a doubt whether these spots consist in reality of arsenic and not of antimony ; for even the characteristic odor of garlic is not sufficient to set at rest every doubt upon this point.   The following methods are best adapted to lead to a positive conviction in this respect.

a. The central part of the tube through which the arseniuretted hydrogen passes, is heated to redness to produce a distinct metallic mirror.   A very feeble stream of dry sulphuretted hydrogen is then transmitted through the tube, and the metallic mirror heated by means of a spirit-lamp, from its outer towards its inner extremity.   If arsenic alone be present, yellow sulphuret of arsenic will be formed within the tube ; if antimony alone be present, an orange or black sulphuret of antimony will be produced ; but if the mirror consist of both metals jointly, the two sulphurets will appear side by side, the sulphuret of arsenic as the more volatile, lying invariably before the sulphuret of antimony.   Not long since, this conversion of antimony and arsenic into sulphurets was suggested as the surest means of distinguishing these two metals from one another.   Experience has, however, taught us that the differences which the two sulphurets exhibit in color and volatility are not striking enough to prevent the possibility of mistakes.   But if dry hydrochloric acid gas be now transmitted without application of heat, through the tube (containing the sulphuret of arsenic, sulphuret of antimony, or both sulphurets together) no alteration whatever will take place if sulphuret of arsenic alone is present, even though the gas be transmitted through the tube for a considerable time.   If sulphuret of antimony alone is present, this will entirely disappear, and if both sulphurets are present, the sulphuret of antimony will immediately volatilize, whilst the yellow sulphuret of arsenic will remain.   If a small quantity of ammonia be then introduced into the tube, the sulphuret of arsenic will be dissolved, and may thus be readily distinguished from sulphur which perhaps may have separated. My personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic.

b. The limb e is turned into a horizontal position, and the gas kindled and made to burn in a glass flask, having a capacity of

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about twelve ounces. This flask is placed in a beaker glass filled with cold water, and is constantly kept turning to prevent its becoming hot. After some time, when the oxygen in the flask is nearly exhausted, and the flame grows feeble, a second flask is substituted for the first, and a third for the second, &c. &c. These flasks now contain, either arsenious acid alone, or oxide of antimony alone, or a mixture of both substances. If the first be the case, the white sublimate obtained will completely dissolve in - hot water, and the solution may then be tested with other re- agents to confirm the presence of arsenic. In the second case nothing will dissolve, nor in the third, if the oxide of anti- mony is present in sufficient quantity, since in that case arsenite of antimony will be formed. The arsenic in this last case may be detected by dissolving the sublimate in a small portion of dilute solution of potassa, and adding to the solution sulphuretted hydro- gen, and afterwards bicarbonate of ammonia in excess. Upon this, the whole of the antimony will precipitate as sulphuret of antimony, whilst the sulphuret of arsenic remains dissolved in the excess of bicarbonate of ammonia, from which it precipitates upon the addition of hydrochloric acid to acid reaction. When arsenic and antimony are both present, this method is inferior to that de- scribed sub *a.*—MARSH was the first who suggested the method of detecting arsenic by the production of arseniuretted hydrogen.

9. If a perfectly dry mixture of arsenious acid, or an arsenite with *carbonate of soda and charcoal*, be introduced into a well- dried glass tube drawn out and closed at one end, and then heated to redness over a spirit-lamp, proceeding from the commencement of the small part towards the closed extremity, the charcoal will oxidise at the expense of the oxygen of the arsenious acid, and arsenic will be liberated, which volatilizes and re-condenses above the heated part of the tube, forming a more or less dark-brown metallic mirror of great lustre. This mirror may be driven along in the tube by heat, and finally altogether expelled, when, upon its volatilization in the air, the character- istic odor of arsenic will afford further confirmation of the presence of this substance. For the reduction of free arseni- ous acid, a fragment of charcoal is used, instead of carbonate of

soda and charcoal ; the arsenious acid is introduced into the drawn-out point of the tube, the fragment of charcoal is pushed over it and ignited, and heat is then applied to the point of the tube. This process has an advantage over the former, that charcoal is less likely to soil the tube than carbonate of soda and charcoal. The non-formation of a metallic mirror, when testing a supposed arsenite with carbonate of soda and charcoal, is not always a positive proof that no arsenic is present, since there are several compounds of arsenious acid, and more particularly those with heavy metallic oxides, e. g. peroxide of iron, which do not yield distinct metallic mirrors : it is therefore necessary to ascertain, first, whether the arsenite in question may not belong to the latter class, before the non-formation of mirror can be considered as a positive proof of the absence of arsenic.

10. Upon fusing arsenious acid, or arsenites, or a sulphuret of arsenic with a mixture of equal parts of dry *carbonate of soda* and *cyanide of* potassium, the whole of the arsenic is invariably reduced to the metallic state, as also the bases if easily reduceable ; the eliminated oxygen converts part of the cyanide of potassium into cyanate of potassa—the eliminated sulphur (in case of sulphurets of arsenic) converts the cyanide into sulphocyanide of potassium. The operation is conducted as follows :— the arsenical compound under examination is introduced, in a state of perfect dryness, into a small glass tube, expanded into a bulb at one end, and then covered with six times its quantity of the dry mixture of carbonate of soda and cyanide of potassium. The whole mass must not fill more than half the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. The heat of a spirit-lamp is then applied to the bulb, and maintained for a while, since the arsenic frequently requires some time for its complete sublimation. The mirrors which are obtained in this process are of exceeding purity. They are produced from all arsenites, the bases of which remain either altogether unreduced, or when converted into metallic arseniurets, lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended on account of its simplicity, and neatness, as well as for the preciseness

of the results attainable by its application, even though but minute
quantities of arsenic be present.   It is more especially adapted for
the direct production of arsenic from sulphuret of arsenic, and is
in this respect superior to all other methods hitherto suggested.
The sensitiveness of this method may be heightened exceedingly
by heating the mixture in a stream of dry carbonic acid gas.   A
series of experiments made by Dr. BABO and myself, has shown
that the most accurate and satisfactory results are to be obtained
in the following manner:—

Plates VI. and VII. illustrate the apparatus in which the pro-
ces is conducted.

PLATE VI.
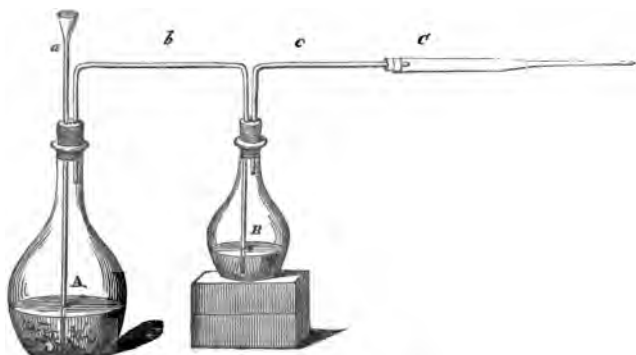
A is a capacious flask intended for the evolution of carbonic
acid ; it is half filled with water and large fragments of limestone
or marble—(chalk does not yield a constant stream of carbonic
acid gas.)—B is a smaller flask containing hydrated sulphuric
acid.   The flask A is closed with a doubly perforated cork, into
the one aperture of which is inserted a funnel-tube (*a*) which
reaches nearly to the bottom of the flask ; into the other perfora-
tion is fitted a tube (*b*) which serves to conduct the evolved gas
into the sulphuric acid in B, when it is thoroughly freed from
moisture.   The tube *c* conducts the dried gas into the reduction
tube C, which is illustrated by

PLATE VII.

This engraving represents the tube on the scale of one-third of its length. When the apparatus is arranged, the perfectly dry sulphuret of arsenic, or arsenite under examination, is to be triturated in a slightly heated mortar with about 12 parts of a dry mixture, consisting of 3 parts of carbonate of soda and 1 part of cyanide of potassium. The powder is placed upon a narrow slip of card-paper bent into the shape of a gutter, and the latter is then pushed into the reduction tube up to *e*; by turning the tube half-way round its axis, the mixture is made to fall down into the tube between *e* and *d*, every other part of the tube remaining perfectly clean. The tube thus prepared is now connected with the gas evolution apparatus, and a moderate stream of carbonic acid is then evolved by pouring some hydrochloric acid into the funnel-tube *a*. The mixture in *e* is now most carefully and thoroughly dried by heating the tube its whole length very gently with a spirit-lamp. When every trace of water is expelled, and the gas-stream has become so slow that the single bubbles pass through the sulphuric acid in B at intervals of one second, the reduction-tube is heated to redness at *g*, by means of a spirit-lamp; as soon as *g* is red hot, the flame of a second and larger spirit-lamp is applied to the mixture, proceeding from *d* to *e* until the whole of the arsenic is reduced and volatilized. The far greater portion of the volatilized arsenic recondenses at *h*, whilst an extremely minute portion only escapes through *i*, imparting to the surrounding air the peculiar odor of garlic. The flame of the second lamp is then slowly and gradually advanced up to *g*, and by this means the whole of the arsenic which may have condensed in the wide part of the tube, is propelled to *h*. When this has been attained, the tube is closed at the point *i* by fusion, and the mirror is then finally driven by the application of heat from *i* towards *h*. In this manner, perfectly distinct metallic

mirrors may be produced from as little as the 1-300th part of a grain of sulphuret of arsenic. Neither sulphuret of antimony nor any other compound of antimony yield metallic mirrors, when treated in this manner.

11. If arsenious acid or an arsenite be exposed on a charcoal support to the *reducing flame of the blow-pipe*, a highly characteristic garlic odor will be perceived, especially if some carbonate of soda be added to the substance examined. This odor has its origin in the reduction and reoxidation of the arsenic, and enables us to detect very minute quantities. This test, however, cannot be implicitly relied on. The garlic odor proceeds neither from the fumes of arsenious acid, nor from those of arsenic, but probably from those of a lower degree of oxidation of the latter substance. Arsenic exhales this odor invariably when heated in the air.

<div align="center">

e. ARSENIC ACID. $(As\,O_5)$.

</div>

1. Arsenic acid is a colorless, or white mass, which gradually deliquesces in the air, and dissolves in water: it fuses at a gentle red-heat without suffering decomposition; but at a higher temperature it is resolved into oxygen and arsenious acid, which volatilizes.

2. Most of the arseniates are insoluble in water. Of the neutral arseniates, those with alkaline bases alone are soluble in water. Most of the neutral and basic arseniates can bear a strong red-heat without suffering decomposition. The acid arseniates lose their excess of acid upon ignition, this excess being decomposed into arsenious acid and oxygen.

3. *Sulphuretted hydrogen* fails to precipitate alkaline and neutral solutions of arseniates; but in acidified solutions it produces a yellow precipitate of SULPHARSENIC ACID, $(As\,S_5)$. This precipitate never forms instantaneously, and in dilute solutions frequently only after the lapse of a considerable time (twenty-four hours). Heat promotes its separation. The sulpharsenic acid manifests the same deportment as the sulpharsenious acid, with the various solvents and decomposing agents which I have mentioned while treating of the latter substance. Sulphurous acid,

when added to a solution of free arsenic acid or of an arseniate, converts the arsenic acid into arsenious acid and sulphuric acid; this change may be promoted by the application of heat. If sulphuretted hydrogen,—and should it be required, an acid be now added to the mixture,—the whole of the arsenic will immediately precipitate as sulpharsenious acid.

4. *Hydrosulphuret of ammonia* converts the arsenic acid in neutral and alkaline solutions of arseniates into sulpharsenic acid, which remains in solution as sulpharsenico-sulphuret of ammonium. Upon the addition of an acid to the solution, this double sulphuret is decomposed, and sulpharsenic acid precipitates. The separation of this precipitate proceeds more rapidly than is the case when acid solutions are precipitated with sulphuretted hydrogen. It is promoted by heat.

5. *Nitrate of silver* produces in neutral solutions of the arseniates highly characteristic reddish-brown precipitates of ARSE-NIATE OF SILVER, (3 Ag O, As O_5), which are soluble both in dilute nitric acid and in ammonia. *Ammonio-nitrate of silver* produces the same precipitate in solutions of arsenic acid or of arseniates, when containing a free acid.

6. *Sulphate of copper* and *ammonio-sulphate of copper* produce, under the same circumstances as the nitrate and ammonio-nitrate of silver, greenish blue precipitates of ARSENIATE OF COPPER. ($\text{As O}_5, 2 \text{ Cu O, H O}$).

7. With *hydrogen, carbonate of soda and charçoal,* and *cyanide of potassium,* before the *blow-pipe,* the arseniates manifest the same deportment as the arsenites.

Recapitulation and remarks.—The separation and positive detection of the oxides belonging to the second section of the sixth group, and especially of peroxide of tin, are sometimes, and under certain circumstances, attended with difficulties. The protoxide of tin, however, may be readily detected by its reaction with perchloride of gold, or with perchloride of mercury, even in the presence of other oxides. The separation of peroxide of tin from oxide of antimony may be effected with tolerable accuracy in the humid way by means of a hot solution of bitartrate of

potassa, or of a solution of free tartaric acid ; but this method is applied with success only when the peroxide of tin exists in the modification produced by the action of nitric acid on metallic tin.   It is necessary, therefore, if the substance under examination is not an alloy, to reduce the compound of tin to the metallic state, either in the humid way, by means of zinc, the presence of nitric acid being carefully avoided—or, in the dry way, by means of cyanide of potassium.   The method of separating antimony from tin in the form of sulphurets, by means of ammonia, is liable to give rise to mistakes, since the higher sulphurets of antimony are soluble in ammonia, and even the protosulphuret of this metal is not quite insoluble in this substance.   The only *positive* proof of the presence of peroxide of tin is the production of a *ductile* metallic grain of tin, in the reducing flame of the blow-pipe, since the ductility of tin distinguishes this metal amply and sufficiently from antimony.   This reduction is very readily effected before the blow-pipe by means of a mixture of equal parts of cyanide of potassium and carbonate of soda ; but care should be taken that the peroxide of tin be not mixed with nitrate of potassa —since this would cause deflagration—nor with any other substance of that description.   Whether the ductile metallic grain produced in the process be *really* tin may be ascertained and confirmed by the following direct experiment ;—the metallic grain is boiled with some concentrated hydrochloric acid, water is added to the solution, and the fluid tested with perchloride of mercury.   Vide § 95, *b*. 7.

Peroxide of tin and oxide of antimony may also be detected and distinguished, side by side, before the blow-pipe, the antimony is characterized by the peculiar incrustation with which its oxide covers the charcoal support, and the peroxide of tin, after the volatilization of the antimony, may be readily recognized by the ductility of the grain of metallic tin produced in the process.   I have, however, found that inexperienced students fail generally in their attempts at detecting peroxide of tin and oxide of antimony, side by side, in this manner.   Antimony may be recognized, moreover, by the decomposition which its chloride suffers by the action of water, and likewise by the color of its sul-

phuret. The latter test, however, is uncertain, if the sulphuret of antimony contain much sulphuret of arsenic in admixture. The best way of arriving at a positive conclusion in such cases is to ignite the mixed sulphurets,—when the sulphuret of arsenic will volatilize—to dissolve the residue in hydrochloric acid, and to test the solution with sulphuretted hydrogen.

The detection of arsenic is not difficult, yet errors will frequently arise, especially if positive and definite conclusions be drawn from individual and isolated reactions, such as the characteristic odor, for instance, which arsenical compounds exhale when heated on charcoal. We must, therefore, lay it down as a rule that the presence of arsenic is to be considered positively proved only by a concurrence of the various reactions, and particularly by the production of metallic arsenic.—Arsenic may be separated from tin with tolerable accuracy by deflagrating the sulphurets of the two metals with carbonate of soda and nitrate of soda. The presence of tin, moreover, does not interfere with the detection of arsenic. But the case is very different with antimony, especially when testing by MARSH's method, which is now so universally adopted. The mere production of a metallic mirror by MARSH's apparatus ought, therefore, never to be looked upon as a positive proof of the presence of arsenic, and additional tests must invariably be had recourse to, to place the presence of this substance beyond all doubt. The method described at § 95, d. 8, a., yields the most positive and precise results in this respect, and is, moreover, exceedingly delicate. A tolerably complete separation of arsenic from antimony may be effected by means of bicarbonate of ammonia, the protosulphuret of antimony being nearly insoluble in this substance, whilst the sulphuret of arsenic dissolves readily in it. But this method of distinguishing between arsenic and antimony yields precise results only when the protosulphuret of antimony is entirely free from any admixture of a higher sulphuret or of free sulphur, and when the proportion of sulphuret of arsenic present is not too inconsiderable. It is, therefore, generally inapplicable for the separation of the sulphurets produced in the usual way.

Those methods of effecting the separation of arsenic from an-

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timony, which are based upon the different deportment of the respective sulphurets of the two metals, with concentrated hydrochloric acid, or with caustic ammonia, yield even less precise results than the method just now described. Nor is a perfect separation of the two metals to be affected by treating with nitric acid, as a portion of the arsenic always remains, as arsenic acid or arsenious acid, combined with the oxide of antimony. A far more precise result may be obtained by deflagrating the sulphurets with carbonate of soda and nitrate of soda, treating the residuary mass with water, filtering the solution, and then decomposing with nitric acid, the small quantity of basic antimoniated alkali present in the filtrate. Nearly the whole of the antimony is obtained in this process, as an insoluble, and the whole of the arsenic as a soluble compound.

The presence of antimony does not interfere with the accuracy of the results obtained by the reduction of arsenites or arseniates, by means of *carbonate of soda and charcoal,* or by means of *cyanide of potassium* and *carbonate of soda.* Arsenious acid and arsenic acid in aqueous solution may be most readily and positively distinguished from one another, by means of nitrate of silver. Should the presence of other substances interfere with the direct application of the test, the solution is to be precipitated completely with sulphuretted hydrogen ; the precipitated sulphurets are then to be dissolved in solution of potassa, and the fluid subsequently boiled either with hydrated oxide or carbonate, or basic nitrate of bismuth ; the fluid is then to be filtered off from the precipitated sulphuret of bismuth, and one portion of the filtrate tested for arsenious acid by means of sulphate of copper, according to the method described § 95, *d.* 7 ; another portion of the filtrate is to be neutralized with nitric acid, and finally tested for arsenic acid, by means of nitrate of silver.

B. DEPORTMENT OF THE ACIDS WITH REAGENTS.

§ 96.

We classify the reagents which serve for the determination of the acids, in the same manner as those used for the determination of

the bases, into GENERAL REAGENTS, i. e. such as indicate the GROUP to which the acid under examination belongs; and SPECIAL REAGENTS, i. e. such as serve to effect the detection of the INDIVIDUAL ACIDS. The groups into which we classify the various acids can scarcely be defined and limited with the same degree of precision as those into which the bases are divided.

The two principal groups into which acids are divided are those of INORGANIC and ORGANIC ACIDS. In this division we have chosen those characteristics by which, irrespectively of theoretical considerations, the ends of analysis are most easily attained. We will, therefore, select here, as the characteristic mark to guide us in the classification into organic and inorganic acids, the deportment which the various acids manifest at a high temperature, and will therefore call *organic* those acids of which the salts— (particularly those which have an alkali or an alkaline earth for base)—are decomposed upon ignition, this decomposition being attended with separation of charcoal.

By selecting this deportment at a high temperature as the distinctive characteristic of organic acids, we are enabled to determine at once by a most simple preliminary experiment the class to which the acid or acids under examination belong. The salts of organic acids with alkalies or alkaline earths are converted into carbonates, upon ignition.

I. INORGANIC ACIDS.

First Group.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY CHLORIDE OF BARIUM : *Arsenious Acid — Arsenic Acid — Chromic Acid—Sulphuric Acid—Phosphoric Acid—Boracic Acid—Oxalic Acid—Hydrofluoric Acid—Carbonic Acid— Silicic Acid.*

This group is again subdivided into four classes, viz.:
1. Acids which are decomposed in acid solutions by sulphuretted

hydrogen, and which have therefore been alluded to already, while treating of the bases, viz., ARSENIOUS ACID, ARSENIC ACID, and CHROMIC ACID.

2. Acids which are not decomposed in acid solutions by sulphuretted hydrogen, and the baryta compounds of which are insoluble in hydrochloric acid. Of the above enumerated acids SULPHURIC ACID alone belongs to this class.

3. Acids which are not decomposed in acid solutions, by sulphuretted hydrogen, and the baryta compounds of which dissolve in hydrochloric acid apparently WITHOUT DECOMPOSITION, inasmuch as the acids cannot be completely separated from the hydrochloric solution, by heating or evaporation ; these are PHOSPHORIC ACID, BORACIC ACID, OXALIC ACID, and HYDROFLUORIC ACID. (Oxalic acid belongs more properly to the organic group. I add this acid, however, here to the inorganic class, since its salts are decomposed upon ignition without leaving a real carbonaceous residue, and are accordingly liable to be confounded with the salts of inorganic acids.)

4. Acids which are not decomposed in acid solutions, by sulphuretted hydrogen, and the baryta salts of which are soluble in hydrochloric acid, WITH DECOMPOSITION, (separation of the acids :) CARBONIC ACID, SILICIC ACID.

First Section of the First Group of the Inorganic Acids.

§ 97.

a. Sulphuretted hydrogen precipitates from acid solutions of ARSENIOUS ACID and ARSENIC ACID, the corresponding sulphurets of these acids. Since this would lead to confounding them rather with the metallic oxides than with other acids, I deemed it more judicious to place these two acids with the oxides of the sixth group, (vide § 95).

b. CHROMIC ACID. (Cr O_3).

1. Chromic acid forms a scarlet-red crystalline mass, or distinct crystals presenting the form of needles. Upon ignition it is resolved into oxide of chromium and oxygen. It deliquesces rapidly

when exposed to the air. It dissolves in water, imparting to this menstruum a deep red-brown tint, which remains visible even when considerably diluted.

2. The chromates are all red or yellow, and for the most part insoluble in water. Some of them are decomposed upon ignition; those with alkaline bases are fixed, and soluble in water; the solutions of the neutral alkaline chromates are yellow, those of the alkaline bichromates are red. These tints are still visible in highly dilute solutions. The yellow color of a neutral solution changes into red on the addition of a mineral acid, owing to the formation of an acid salt.

3. *Sulphuretted hydrogen* reduces chromic acid, no matter whether present in solution in the free state or as a chromate; oxide of chromium, water, and sulphuric acid, are formed in this process, and sulphur precipitates. Heat promotes this decomposition. When no free acid is present, a portion only of the reduced oxide of chromium is retained in solution by the newly-formed sulphuric acid, and a greenish-grey precipitate is produced consisting of a mixture of hydrated oxide of chromium with sulphur. But if free acid is present, the precipitate is far less considerable and consists of pure sulphur. The salt of oxide of chromium formed imparts a green tint to the fluid, in either case.

4. Chromic acid may also be reduced to chromic oxide by means of many other substances besides sulphuretted hydrogen, more particularly by *sulphurous acid,* or by heating with *hydrochloric acid,* especially upon the addition of alcohol, (when hydrochloric ether and aldehyde are evolved,) also by *metallic zinc,* or by heating with *tartaric acid, oxalic acid,* &c. All these reactions are clearly characterized by the transition of the red or yellow color of the solution to the green tint of the reduced salt of oxide of chromium.

5. *Chloride of barium* produces a yellowish white precipitate of CHROMATE OF BARYTA (Ba O, Cr O_3) which is soluble in dilute hydrochloric and nitric acids.

6. *Nitrate of silver* produces a dark purple-red precipitate of CHROMATE OF SILVER (Ag O, Cr O_3) which is soluble in nitric acid and in ammonia.

7, *Acetate of lead* produces a yellow precipitate of CHROMATE
OF LEAD (Pb O, Cr O₃,) which is soluble in potassa, and sparingly
soluble in dilute nitric acid. The yellow color of this precipitate
changes to red, upon heating with ammonia.

8. When insoluble chromates are fused with *carbonate of soda*
and nitrate of potassa, and the fused mass is treated with
water, the fluid produced appears YELLOW from the alkaline
chromate which it holds in solution; upon the addition of an
acid, this yellow color changes to red. The oxides remain either
in their pure state or as carbonates.

Remarks.—When testing for bases we always find the chromic
acid as chromic oxide, since sulphuretted hydrogen reduces the
acid to the state of oxide. The characteristic color of the solution
frequently renders the application of any further test unnecessary.
If there is reason to suppose that chromic acid is present in a
solution, metallic oxides being also present, it is preferable to
effect the reduction of the chromic acid, by means of hydrochloric
acid and alcohol, or by sulphurous acid, instead of reducing it
with sulphuretted hydrogen. The reactions with salts of silver
and salts of lead afford a positive and confirmatory proof of the
presence of chromic acid in aqueous solutions.

Second Section of the First Group of the Inorganic Acids.

§ 98.

SULPHURIC ACID. (S O₃).

1. Anhydrous sulphuric acid is a white feathery-crystalline mass
which emits strong fumes upon exposure to the air; hydrated sul-
phuric acid forms an oily liquid, colorless and pellucid like water.
Both the anhydrous and hydrated acid carbonize organic sub-
stances, and combine with water in all proportions, the process of
combination being attended with considerable elevation of tem-
perature.

2. Most of the sulphates are soluble in water; the insoluble
sulphates are generally white; the soluble sulphates are for the
most part colorless, in their crystalline state. The sulphates

of the alkalies and alkaline earths are not decomposed upon ignition.

3. *Chloride of barium* produces even in highly dilute solutions of sulphuric acid and of the sulphates, a heavy white precipitate of SULPHATE OF BARYTA (Ba O, SO₃) in the form of a fine powder; this precipitate is insoluble in hydrochloric acid and in nitric acid.

4. *Acetate of lead* produces a heavy, white precipitate of SULPHATE OF LEAD (Pb O, SO₃) which is sparingly soluble in dilute nitric acid, but dissolves completely in hot concentrated hydrochloric acid.

5. The salts of sulphuric acid with the alkaline earths which are insoluble in water and acids, are converted into CARBONATES by fusion with *alkaline carbonates.* But the sulphate of lead is reduced to the state of PURE OXIDE when treated in this manner. Both the conversion of the former into carbonates, and the reduction of the latter to the state of oxide, are attended with the formation of an alkaline sulphate.

6. Upon fusing sulphates with *carbonate of soda and charcoal,* on the loop of a platinum wire, in the inner flame of the blow-pipe, the sulphuric acid is reduced, and sulphuret of sodium formed, which may be readily recognized by the odor of sulphuretted hydrogen emitted by the bead when moistened with an acid. If the process of moistening the bead be performed upon a piece of paper drenched with solution of lead, or upon a clean silver plate, (such as a polished coin,) a black stain of sulphuret of lead or sulphuret of silver will immediately form upon the paper or coin.

Remarks.—The characteristic and exceedingly delicate reaction of sulphuric acid with salts of baryta renders the detection of this acid an easier task than that of almost any other. It is simply necessary to take care not to confound with sulphate of baryta, precipitates of chloride of barium, and particularly of nitrate of baryta, which are formed upon mixing aqueous solutions of these salts with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from sulphate of baryta, since they redissolve immedi-

ately upon diluting the acid fluid with water. The deportment of sulphuric acid with baryta might, however, lead to confounding this acid with hydrofluosilicic acid. Although we do not treat of the latter substance in the present work, yet it may be as well to remark that, should any doubt arise as to a precipitate of baryta, this may be easily set at rest by fusing the precipitate in question in the inner flame of the blow-pipe, with carbonate of soda and charcoal. (Compare § 98, 6).

Third Section of the First Group of the Inorganic Acids.

§ 99.

a. PHOSPHORIC ACID. (PO_5).

We shall treat here only of tribasic phosphoric acid, since it is this form of the acid and its salts which are used in pharmacy and occur in nature; monobasic and bibasic acids we pass by. It may here, however, be observed, that very many of the mono and bibasic phosphates, in boiling with strong acids, and especially by warming with concentrated sulphuric acid, are so far altered as to be converted into a tribasic salt. When fused with carbonate of soda the phosphates are all rendered tribasic.

1. The hydrate of common phosphoric acid $(PO_5, 3 HO)$ forms colorless and pellucid crystals which deliquesce rapidly in the air, forming a syrupy non-caustic fluid. The action of heat changes it into hydrated pyro, or meta-phosphoric acid, according as either one or two equivalents of water are expelled.

2. The action of heat fails to decompose the phosphates with fixed bases, but converts them into pyrophosphates when, containing one equivalent of basic water, and into metaphosphates, when containing two equivalents of basic water. The phosphates with alkaline bases alone are soluble in water in the neutral state. The solutions manifest an alkaline reaction.

3. *Chloride of barium* produces in aqueous solutions of the neutral or basic phosphates, a white precipitate of PHOSPHATE OF BARYTA $[PO_5, 2 Ba O, HO,$ or $PO_5, 3 Ba O]$* which is in-

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* Precipitates of the first composition are formed in solutions containing

soluble in hydrochloric acid and in nitric acid, and difficultly soluble in chloride of ammonium.

4. *Solution of sulphate of lime* produces in neutral or alkaline solutions of phosphates, a white precipitate of PHOSPHATE OF LIME (PO_5, 2 Ca O, HO, or PO_5, 3 Ca O) which dissolves readily in acids, even in acetic acid.

5. *Chloride of magnesium* or *sulphate of magnesia* produces in neutral solutions of phosphates, white precipitates of PHOSPHATE OF MAGNESIA (PO_5, 2 Mg O, HO) which are, however, visible only in rather concentrated solutions, and particularly upon the application of heat. But if some chloride of ammonium and *free ammonia* or *carbonate of ammonia* be added to the solution, the chloride of magnesium or sulphate of magnesia, will produce in even highly dilute solutions, a white, crystalline and quickly subsiding precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA (PO_5, 2 Mg O, NH_4 O) which is insoluble both in ammonia and chloride of ammonium, but dissolves readily in acids, even in acetic acid, This precipitate appears often only after the lapse of some time; stirring and agitation promotes its separation, vide § 87, *d.* 7. In solutions of phosphates with three equivalents of fixed base, salts of magnesia produce immediately a precipitate of basic phosphate of magnesia (PO_5, 3 Mg O) and this even though the solution be dilute.

6. *Nitrate of silver* throws down from solutions of neutral and basic alkaline phosphates, a light yellow precipitate of PHOSPHATE OF SILVER. ($P O_5$, 3 Ag O). If the solution contained a basic phosphate, the fluid in which the precipitate is suspended, will manifest a neutral reaction, whilst the reaction will be acid, if the solution contained a neutral phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid receives for the three equivalents of oxide of silver, which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water; and as the latter does not neutralize the acid properties of the nitric acid the solution becomes acid.

an alkaline phosphate with two equivalents of a fixed base or ammonia; whilst precipitates of the latter composition are formed in solutions which contain an alkaline phosphate, with three equivalents of a fixed base or ammonia.

7. *Acetate of lead* produces in neutral and alkaline solutions of phosphates a white precipitate of PHOSPHATE OF LEAD, (P O$_5$, 3 Pb O), which is readily soluble in nitric acid, but nearly insoluble in acetic acid. This reaction acquires a very great value as a test for phosphoric acid, from the peculiar deportment which the precipitated phosphate of lead exhibits before the blow-pipe. For, in the first place, even the inner flame of the blow-pipe fails to reduce it, or effects its reduction only with the greatest difficulty, and, in the second place, the colorless and transparent bead which it yields in the oxidizing flame turns opaque upon cooling, and crystallizes generally into perfectly distinct dodecahedrons.

8. If to a solution containing phosphoric acid, no matter in whatever form or combination, hydrochloric acid be added to acid reaction, and afterwards one or two drops of *perchloride of iron*, and finally *acetate of potassa* in excess, a floculent gelatinous white precipitate of *perphosphate of iron* (3 P O$_5$, 2 Fe$_2$, O$_3$, 3 H O) will be invariably produced under all circumstances. Should more perchloride of iron have been added than corresponds to the amount of phosphoric acid present, the fluid in which the precipitate is suspended, will appear red ; otherwise it will appear colorless. Should the quantity of phosphoric acid present be very minute, the precipitate will become distinctly visible only after from 12 to 24 hours' standing. Upon the requisite proportion of perchloride of iron being added depends the sensibility of this reaction, the perphosphate of iron not being absolutely insoluble in a solution of per-acetate of iron. It is well adapted for the detection of phosphoric acid in general, and more particularly when we have to deal with acid solutions of phosphates of the alkaline earths. The perfect and complete separation of the alkaline earths from the phosphoric acid, is best effected by the following process. Hydrochloric acid is added to the solution of the phosphate under examination, until the fluid manifests an acid reaction, and as much perchloride of iron is then added as will cause the fluid to turn red upon the addition of acetate of potassa in excess; the mixture is then boiled, which will cause the whole of the peroxide of iron and phosphoric acid to precipitate; the fluid is finally filtered off from the precipitate. The filtrate,

which is colorless, contains the whole of the alkaline earths as chlorides.

9. If a small quantity of phosphoric acid exists in combination with a large quantity of peroxide of iron, the mass must be finely powdered, fused with carbonate of soda, and then exhausted with water. The solution contains the phosphoric acid in combination with the soda. If, however, as is generally the case with iron stone, ochreous earths, &c., alkaline earths are at the same time present, the following method is to be observed: the phosphoric acid compound, freed from silica, arsenic acid, and alumina, is dissolved in hydrochloric acid, heated to the boiling point, and sulphite of soda added until the solution is colorless, when all the persalt of iron will be converted into protosalt; the excess of sulphurous acid is expelled by ebullition, and the free acid in the solution nearly neutralized by carbonate of soda. Acetate of soda is afterwards added, and finally a drop of perchloride of iron, when, if phosphoric acid be present, a white precipitate of perphosphate of iron will be formed; the perchloride of iron is added until the solution becomes of a reddish color, and after boiling, the whole of the phosphoric acid will be found in the precipitate. This reaction is based on the insolubility of phosphate of iron in the protoacetate of iron, whilst it dissolves in the peracetate. The precipitate thus obtained may be still further tested by dissolving it in hydrochloric acid, and decomposing it with ammonia and hydrosulphuret of ammonia; the filtrate will contain the phosphate of ammonia, which may be determined by treating with a salt of magnesia.

10. If phosphoric acid exists in combination with alumina, either of the following methods may be resorted to for its determination.

a. The hydrochloric acid solution is neutralized with carbonate of soda and excess of carbonate of baryta added, after which the mixture is treated with excess of caustic potassa or soda, and boiled. The alumina now remains in solution, whilst the phosphoric acid forms insoluble phosphate of baryta, which, after dissolving in hydrochloric acid, may be readily decomposed by sulphuric acid.

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b. The hydrochloric acid solution is decomposed by tartaric acid, and treated with excess of ammonia; finally to the clear liquid, chloride of ammonium and sulphate of magnesia are added, when, either at once, or after a short time, a crystalline precipitate is formed; it cannot, however, be considered a positive proof of the presence of phosphoric acid, the tartrate of magnesia in the absence of phosphoric acid having a tendency to form a similar precipitate; as a further proof, this must be heated to redness, the residue dissolved in hydrochloric acid and boiled for some time; if phosphoric acid be present a crystalline precipitate of ammonio-phosphate of magnesia will be produced, when the solution is treated with excess of ammonia.

b. BORACIC ACID. (B O₃).

1. Boracic acid, in its anhydrous state, is a colorless glass, when hydrated it is a porous white mass; in the crystalline state it presents small scaly laminæ, It is soluble in water and alcohol;—the solutions redden litmus paper, but color turmeric paper brown. The borates are not decomposed upon ignition; those with alkaline bases alone are readily soluble in water. The solutions are colorless, and all of them, even those of the acid salts, manifest alkaline reaction.

2. *Chloride of barium* produces in solutions of borates, when not too highly dilute, a white precipitate of BORATE OF BARYTA, (Ba O, B O₃), which is soluble in acids and ammoniacal salts.

3. *Nitrate of silver* produces in rather concentrated solutions of borates, a white precipitate of BORATE OF SILVER, (Ag O, B O₃), which is soluble in nitric acid, and in ammonia.

4. If *sulphuric acid* or *hydrochloric acid* be added to highly concentrated hot solutions of alkaline borates, the BORACIC ACID will separate upon cooling, in the form of shining crystalline scales.

5. If alcohol be poured over free boracic acid or a borate— (in the latter case the boracic acid is to be liberated by the addition of sulphuric acid, which should be used concentrated and in sufficient quantity)—and the mixture be ignited, the flame will appear of a very distinct YELLOWISH-GREEN color, especially

upon stirring the mixture ; this tint is owing to the ignition of the evaporating boracic acid, in its passage through the flame. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, igniting the alcohol, allowing it to burn for a short time, extinguishing the flame, and rekindling it. At the first flickering of the flame its borders will now appear green, even though the quantity of the boracic acid be so minute that it fails to produce a perceptible coloring of the flame, when treated in the usual manner.

$$c. \text{ OXALIC ACID.}   (2 \, C \, O + O = C_2 \, O_3 = \overline{O}).$$

1. The hydrate of oxalic acid is a white powder; the crystallized acid forms colorless rhombic columns. Both the hydrate and the crystallized acid dissolve readily in water and in alcohol. When heated rapidly in open vessels, part of the hydrated acid undergoes decomposition, whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating, and provoke coughing.

2. The whole of the oxalates undergo decomposition at a redheat, the oxalic acid being resolved into carbonic acid and carbonic oxide. Those which have an alkali or an alkaline earth for base, are in this process converted into carbonates (without separation of charcoal, when pure) ; those with metallic base leave either the pure metal or the oxide behind, according to the greater or less degree of reducibility of the metallic oxide. The alkaline oxalates, and also some of the oxalates with metallic bases, are soluble in water.

3. *Chloride of barium* produces in neutral solutions of oxalates, a white precipitate of OXALATE OF BARYTA, (Ba O, $\overline{O}$), which is soluble in nitric acid and in hydrochloric acid, but dissolves more sparingly in ammoniacal salts than borate of baryta.

4. *Nitrate of silver* produces in neutral solutions of oxalates, a white precipitate of OXALATE OF SILVER, (Ag O, $\overline{O}$), which is soluble in nitric acid and in ammonia.

5. *Lime-water*, and all the *soluble salts of lime*, and consequently *solution of sulphate of lime*, produce in even highly

dilute solutions of free oxalic acid or of oxalates, white pulverulent precipitates of OXALATE OF LIME, (Ca O, Ō), which dissolve readily in hydrochloric acid and in nitric acid but are nearly insoluble in oxalic acid and in acetic acid. The presence of ammoniacal salts does not interfere with the formation of these precipitates. The addition of ammonia promotes the precipitation of the free oxalic acid by salts of lime.

6. When hydrated oxalic acid or an oxalate in a dry state is heated with an excess of *concentrated sulphuric acid*, the latter withdraws from the oxalic acid its constitutional water, and thus causes its decomposition into CARBONIC ACID and CARBONIC OXIDE ($C_2 O_3 = C O + C O_2$), which two gases escape with effervescence. If the quantity operated upon is not too minute, the escaping carbonic oxide gas may be kindled; it burns with a blue flame. Should the sulphuric acid acquire a dark tint in this reaction, this is a sign that the oxalic acid examined contained some organic substances in admixture.

d. HYDROFLUORIC ACID. (Fl H).

1. Hydrofluoric acid is a colorless, highly volatile fluid of pungent odor; it emits fumes when exposed to the air, and is miscible with water in all proportions. Hydrofluoric acid is distinguished from all other acids by the exclusive property it possesses to dissolve crystallized silicic acid, and also those of the silicates which are insoluble in hydrochloric acid. Fluoride of silicon and water are formed in the process of solution. ($Si O_2 + 2 Fl H = Si Fl_2 + 2 H O$). Hydrofluoric acid decomposes with metallic oxides, in the same manner, viz., to metallic fluorides and water.

2. The alkaline fluorides are soluble in water, whilst those with the metals of the alkaline earths are either altogether insoluble, or dissolve in this menstruum with very great difficulty. Fluoride of aluminum is readily soluble. Most of the fluorides corresponding with the oxides of the heavy metals are very sparingly soluble in water; this is the case, for instance, with fluoride of copper, fluoride of lead, fluoride of zinc; many other fluorides dissolve in water without difficulty, such are, for instance, the perfluoride of iron, protofluoride of tin, perfluoride of mercury, &c. Of those

compounds which are either insoluble or but sparingly soluble in water, many dissolve in free hydrofluoric acid, whilst others remain undissolved in this menstruum.   Most of the fluorides bear ignition in a crucible without suffering decomposition.

3. *Chloride of calcium* produces in aqueous solutions of hydrofluoric acid or of fluorides, a gelatinous precipitate of FLUORIDE OF CALCIUM (Ca Fl), which is so transparent, as at first to induce the belief, that the fluid has remained perfectly clear and unaltered.   The addition of ammonia promotes the complete separation of the precipitate.   The precipitated fluoride of calcium is insoluble in hydrochloric acid, and nitric acid, and also in alkaline fluids in the cold ; a trace of it dissolves, however, upon boiling with hydrochloric acid.   It is scarcely more soluble in free hydrofluoric acid, than in water.

4. If any finely-levigated fluoride be mixed with powdered *glass* or *sand*, the mixture drenched in a test tube, with *concentrated sulphuric acid*, and heat applied, FLUOSILICIC GAS will be evolved, which will form dense white fumes in moist air.   If this gas be transmitted through water—(by means of a bent tube fitted to the test-glass)—the hydrate of silicic acid will separate as a gelatinous mass, and hydrofluosilicic acid will be formed, which latter imparts a strongly acid reaction to the fluid.   Compare § 46. When operating upon very minute quantities, it is advisable to transmit the gas simply through a glass tube, moistened within, when the evolution of fluosilicic gas will be clearly indicated by the separation of silicic acid, which impairs the transparency of the tube in its whole length.

5. If the solution of a fluoride, mixed with sulphuric acid, be poured over a glass plate, coated with bees-wax, which has here and there been removed by means of a pointed instrument,* and the fluid be allowed to dry upon the plate, the exposed lines

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* The coating of the plate may be readily effected by melting some wax upon it, and allowing the fused mass to spread equally over the surface ; the instrument used for tracing the exposed lines should not be too hard ; a pointed piece of wood answers the purpose best.   The subsequent removal of the wax is effected by heating the plate, wiping the fused mass off, and washing the plate with oil of turpentine.

will, upon the removal of the wax, be found etched into the glass. When operating upon very minute quantities, the mixture of the fluoride with sulphuric acid may be simply poured into a watch-glass, and evaporated to dryness, at a gentle heat, when, upon the removal of the residue with water, the internal surface of the glass will appear dimmed.

6. If a finely-powdered fluoride, no matter whether soluble or insoluble, be drenched in a platinum crucible with concentrated sulphuric acid, the crucible covered with a glass plate, prepared as directed at 5, and then exposed to a gentle heat for the space of from fifteen to thirty minutes, the exposed lines will, upon the removal of the wax, be found etched into the glass. Care must be taken in this process to prevent the melting of the wax ; it is advisable for this purpose to keep the upper surface of the plate moistened with water. If the quantity of hydrofluoric acid dis-engaged by the sulphuric acid be very minute, the etching will frequently be altogether invisible upon the removal of the wax ; it will, however, in such cases reappear when the plate is breathed upon. This reappearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess.

Remarks.—The third section embraces phosphoric acid, boracic acid, oxalic acid, and hydrofluoric acid. We have seen that the baryta compounds of these acids are dissolved by hydrochloric acid, apparently without undergoing decomposition ; alkalies therefore reprecipitate them unaltered, by neutralizing the hy-drochloric acid. The baryta compounds of arsenious acid, arsenic acid, and chromic acid present, however, the same deportment, and must therefore, if present, be removed before any conclusion regarding the presence of phosphoric acid, boracic acid, oxalic acid, or hydrofluoric acid, can be drawn from this reprecipitation of a salt of baryta by alkalies. But even leaving this point alto-gether out of the question, no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less still as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric

solutions the salts of baryta in question, and more particularly the borate of baryta, whenever the solution contains any considerable proportion of free acid, or of an ammoniacal salt. Boracic acid may be invariably detected by the characteristic tint which it communicates to the flame of alcohol, provided care be taken to concentrate the solution sufficiently before adding the alcohol, and in the case of borates, to mix the solution with a sufficient amount of sulphuric acid, (concentrated sulphuric acid answers the purpose best). Upon evaporating solutions of free boracic acid, the acid is to be combined with an alkali, since otherwise a large portion of it will volatilize with the aqueous vapors. Phosphoric acid is sufficiently characterized by the yellow precipitate of phosphate of silver, by the characteristic properties of the basic phosphate of magnesia and ammonia, (more particularly the insolubility of this compound in chloride of ammonium,) by the deportment of phosphate of lead before the blow-pipe, and finally and more particularly by the reaction with perchloride of iron and acetate of potassa. In employing this last reaction, it must not be forgotten that the perphosphate of iron is slightly soluble both in excess of peracetate of iron and in acetate of alumina. Oxalic acid may always be readily detected by solution of sulphate of lime; it is only necessary to bear in mind that the precipitated oxalate of lime does not redissolve in acetic acid, but is readily soluble in dilute hydrochloric acid, and changes upon ignition, to carbonate of lime, differing in this from fluoride of calcium. The oxalates of the alkaline earths are completely decomposed by boiling with carbonate of soda. Finally, hydrofluoric acid cannot readily be confounded with other acids; the reaction described at *d*. 4. affords the most positive test and proof of the presence of this acid. The reaction described at *d*. 5. and 6. are applicable only in the absence of silicic acid; this is to be borne in mind when testing for hydrofluoric acid.

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Fourth Section of the First Group of the Inorganic Acids.

§ 100.

a. CARBONIC ACID.　($C\ O_2$).

1. Carbonic acid at the common temperature and common atmospheric pressure is a colorless gas of far greater specific gravity than atmospheric air, so that it may be poured from one vessel into another. It dissolves in water; the solution has a feebly acid pungent taste ; upon application of heat, the carbonic acid escapes.

2. Part of the carbonates lose their carbonic acid upon ignition; those with colorless oxides are white or colorless. Of the neutral carbonates, only those with alkaline bases are soluble in water. The solutions manifest a very strong alkaline reaction. The bicarbonates with alkaline bases are soluble in water, and also those of the alkaline earths and some of the bicarbonates with metallic bases.

3. The carbonates are decomposed by all free *acids* soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. The decomposition of the carbonates by acids is attended with EFFERVESCENCE, the carbonic acid being disengaged as a colorless and almost inodorous gas which imparts a transient reddish tint to litmus paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkaline bases, since the formation of bicarbonates will frequently prevent effervescence, if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid, by this method, should first be drenched with water to prevent any mistake which might arise from the escape of air-bubbles upon treating the dry substance with the test-acid. Should it be desirable to determine by a direct experiment whether the disengaged gas is really carbonic acid or not, this may be readily accomplished by transferring some of the disengaged gas (but none of the fluid) from the test-cylinder into another tube, adding some lime-water to it, and agitating. The formation of a copious precipitate will prove that the evolved gas is really carbonic acid.

4. *Lime-water* and *water of baryta*, when brought into contact with carbonic acid or with soluble carbonates, produce white precipitates of neutral CARBONATE OF LIME $(Ca\ O,\ C\ O_2)$, or neutral CARBONATE OF BARYTA, $(Ba\ O,\ C\ O_2)$. When testing for free carbonic acid, these reagents ought always to be added in excess, since the acid carbonates of the alkaline earths are soluble in water. The precipitated carbonates of lime and baryta dissolve in acids, with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition.

5. *Chloride of calcium* and *chloride of barium* immediately produce in solutions of neutral alkaline carbonates, precipitates of CARBONATE OF LIME or of CARBONATE OF BARYTA ; in dilute solutions of bicarbonates these precipitates are formed only upon ebullition ; with free carbonic acid these reagents yield no precipitate.

b. SILICIC ACID. $(Si\ O_2)$.

1. Silicic acid is met with in two modifications, crystalline and amorphous. It is insoluble in water and acids, excepting the hydrofluoric acid ; whilst its hydrate is soluble, though in very different degrees, according to the process by which it is obtained. Both amorphous and hydrated silicic acid dissolve in a hot solution of the caustic and carbonated fixed alkalies, but the crystallized acid is insoluble or nearly so. The amorphous is converted into the insoluble (crystalline) by the action of a red heat; if this is now fused with a caustic alkali or an alkaline carbonate, a basic silicate of the alkali is obtained, soluble in water; from this compound, acids again separate hydrated silicic acid. The alkaline silicates only are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids ;* when the solutions are highly concentrated, the hydrate of SILICIC ACID separates in the form of gelatinous flakes, whilst it remains dissolved in more dilute solutions. If a dilute solution of an alkaline silicate be mixed with an acid, (hydrochloric acid or nitric acid,) and the mixture subsequently evaporated to dryness, the hydrated silicic acid is converted into the anhydrous

acid (amorphous), which will remain as a white gritty powder
when the residue is treated with water. The addition of chloride
of ammonium to solutions of alkaline silicates also causes precipi-
tation of hydrated silicic acid.

3. In the silicates with earthy or metallic bases, the silicic acid
exists also either in its soluble or in its insoluble modification.
The silicates with the soluble modification are decomposed by
boiling hydrochloric or nitric acid, the silicic acid separating as
gelatinous hydrate, whilst the decomposing acid combines with
the base. But these acids fail to act upon silicates with the in-
soluble modification of silicic acid. To effect the separation of
the silicic acid from silicates of the latter description, these are to
be treated either in the humid way with hydrofluoric acid, or fused
with alkaline carbonates.

4. *Carbonate of soda* dissolves a copious amount of silicic acid
in the flame of the blow-pipe to colorless beads of SILICATE OF
SODA, which remain transparent on cooling ; the carbonic acid
escapes with effervescence in this process. Inexperienced students
often fail to produce a clear bead, because they use too much
carbonate of soda in proportion to the quantity of the test-
specimen.

5. *Phosphate of soda and ammonia* fails nearly altogether to
dissolve silicic acid. The silicic acid floats about in the trans-
parent bead as an opaque mass, and may therefore be seen better
in the fused than in the cold bead. The silicates show the same
deportment ; the phosphate of soda and ammonia withdraws their
base from them, and separates silicic acid. The bases are
generally dissolved, whilst the silicic acid remains undissolved.

Recapitulation and remarks.—Carbonic acid is generally very
easily detected by the nearly inodorous gas which is evolved when
the carbonates are treated with acids. When operating upon
compounds which, besides carbonic acid, evolve other gases, the
disengaged gas is to be tested with lime water or with water of
baryta. Silicic acid in its soluble modification, (into which it
must invariably be converted,) may be positively detected, under
all circumstances, by supersaturating its compounds with hydro-

chloric acid, evaporating to dryness, treating the residue with water, and testing the undissolved part before the blow-pipe.

Second Group of Inorganic Acids.

ACIDS WHICH ARE PRECIPITATED BY NITRATE OF SILVER, BUT NOT BY CHLORIDE OF BARIUM : *Hydrochloric Acid—Hydrobromic Acid—Hydriodic Acid—Hydrocyanic Acid—Hydrosulphuric Acid.*

§ 101.

The silver compounds corresponding to the acids of this group are insoluble in dilute nitric acid. The acids of this group decompose with metallic oxides; the metals combine with the chlorine, bromine, cyanogen, iodine, or sulphur, whilst the oxygen of the metallic oxides forms water with the hydrogen of the hydracids.

a. HYDROCHLORIC ACID.   (Cl H).

1. Hydrochloric acid, at the common temperature and common atmospheric pressure, is a colorless gas which forms dense fumes in the air, is suffocating and very irritant, and dissolves in water with exceeding facility. The solution (common hydrochloric acid) loses a large portion of its gas upon heating.

2, The neutral chlorides are readily soluble in water, with the exception of chloride of lead, chloride of silver, and protochloride of mercury; most of the chlorides are colorless. Many of them volatilize at a high temperature, without suffering decomposition; many of the chlorides decompose upon ignition, and but few of them are fixed.

3. *Nitrate of silver* produces in even highly dilute solutions of free hydrochloric acid or of metallic chlorides, white precipitates of CHLORIDE OF SILVER, (Ag Cl), which, when exposed to light, turn first violet, and subsequently black, are insoluble in nitric acid, but dissolve readily in ammonia, and fuse without decomposition, when heated.   (Vide § 91, *a.* 5).

4. *Protonitrate of mercury* and *acetate of lead* produce in solutions containing free hydrochloric acid or chlorides, precipitates of PROTOCHLORIDE OF MERCURY (Hg_2 Cl) and CHLORIDE OF

LEAD (Pb Cl).   For the properties of these precipitates, vide § 9 J, *b. 5*, and *c. 6*.

5. When chlorides are heated with *peroxide of manganese* and *sulphuric acid*, chlorine is evolved, which may be readily recognized by its odor and YELLOWISH-GREEN color.

6. If a mixture of a chloride with *chromate of potassa*, be treated with *concentrated sulphuric acid*, in a tubulated retort, at a gentle heat, a deep brownish-red gas will be copiously evolved; (CHROMATE OF PERCHLORIDE OF CHROMIUM, $Cr\ Cl_3$, $2\ Cr\ O_3$); this gas condenses into a fluid of the same color, and passes over into the receiver.   If this chromate of perchloride of chromium is mixed with ammonia in excess, a yellow-colored liquid is produced; the yellow tint is imparted to the fluid by the chromate of ammonia which forms in this process; upon the addition of an acid, the yellow color of the solution changes to a reddish-yellow, owing to the formation of acid chromate of ammonia.

b. HYDROBROMIC ACID.   (Br H).

1. Hydrobromic acid gas, its aqueous solution, and the metallic bromides, offer in their general deportment a great analogy with the corresponding chlorides.

2. *Nitrate of silver* produces in aqueous solutions of hydrobromic acid and bromides a yellowish-white precipitate of BROMIDE OF SILVER, (Ag Br), which changes to violet upon exposure to the light; this precipitate is insoluble in dilute nitric acid, and somewhat sparingly soluble in ammonia.

3. *Nitric acid* decomposes hydrobromic acid and the bromides, —(with the exception of bromide of silver and perbromide of mercury,)—upon the application of heat, and liberates the bromine, by oxidizing the hydrogen or the metal.   The liberated bromine colors the solution yellowish-red.   When operating upon bromides in the solid state, yellowish-red vapors of bromine gas escape, emitting the odor of chlorine; these vapors, when evolved in sufficient quantity, condense in the cold part of the test-tube into small drops.

4. *Chlorine gas,* or *solution of chlorine,* liberates bromine

also in the solutions of its compounds; the fluid assuming a yellowish red tint, if the quantity of the bromine present is not too minute. If a solution of this kind be agitated with some *ether*, it will lose its color, the whole of the bromine present dissolving in the ether, which will now appear distinctly yellow, even though but a very minute quantity of bromine be present. If the ethereal solution of bromine be now agitated with some solution of potassa, the yellow tint will again disappear, owing to the formation of bromide of potassium and bromate of potassa. Upon evaporation, and subsequent ignition of the residue, the bromate of potassa is converted into bromide of potassium, and this may then be further tested as directed at 5.

5. If bromides are heated with *peroxide of manganese* and *sulphuric acid*, YELLOWISH-RED VAPORS OF BROMINE are evolved. If the bromine is present only in a very minute quantity, the color of these vapors may not be visible. The experiment is, in that case, to be conducted in a small retort, and the evolved vapors are to be transmitted through a long condensing glass tube, and finally received into small test-glasses, containing some moistened starch.

6. When moist *starch* is brought into contact with free bromine, no matter whether in solution or in the gaseous state, YELLOW BROMIDE OF STARCH is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by hermetically closing the test-tube which contains the starch drenched with the fluid under examination, and subsequently inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the fluid occupies the bottom. The presence of even the slightest trace of bromine after the lapse of from 12 to 24 hours, will now impart a yellow tint to the starch, which will finally disappear after some time.

7. If a mixture of a bromide with *chromate of potassa* be drenched with sulphuric acid, and heat applied, a brownish-red gas will be evolved, in the same manner as is the case with the chlorides. But this gas consists of pure BROMINE, and therefore the fluid passing over, will not turn yellow, but become colorless, upon supersaturation with ammonia.

c. HYDRIODIC ACID. (I H).

1. Hydriodic acid gas resembles hydrochloric and hydrobromic acid gas, it dissolves copiously in water. The colorless hydrated hydriodic acid turns speedily to a reddish-brown when in contact with the air; this is owing to the formation of hydriodous acid $(I_2 H)$ and water.

2. The iodides also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, far more are insoluble in water than is the case with the corresponding chlorides. Many iodides show characteristic colorations.

3. Nitrate of silver produces in aqueous solutions of hydriodic acid and of IODIDES, yellowish white precipitates of IODIDE OF SILVER, (Ag I), which blacken on exposure to light; these precipitates are insoluble in dilute nitric acid, and but very sparingly soluble in ammonia.

4. A solution of one part of *sulphate of copper*, and two and a quarter parts of *protosulphate of iron*, throws down from aqueous neutral solutions of the iodides, PROTIODIDE OF COPPER, $(Cu_2 I)$, in the form of a dirty-white precipitate. The addition of some ammonia promotes the complete precipitation of the iodine Chlorides and bromides are not precipitated by this reagent, (sulphate of copper and protosulphate of iron.)

5. *Nitric acid* decomposes the hydriodic acid and the iodides in the same manner as the corresponding bromides. Colorless solutions of hydriodic acid or of the iodides acquire therefore immediately a brownish-yellow tint upon the addition of nitric acid, even in the cold ; and from concentrated solutions the IODINE separates as a black precipitate, whilst nitric oxide gas escapes with effervescence. Solid iodides, when heated with nitric acid, evolve, besides nitric oxide gas, VIOLET vapors of iodine, which condense upon the colder parts of the vessel into a blackish sublimate.

6. *Chlorine gas*, and *solution of chlorine*, liberate iodine also from the iodides, but the free iodine combines with these reagents when added in excess, to colorless CHLORIDE OF IODINE.

7. If iodides are heated with concentrated *sulphuric acid*, or with *sulphuric acid* and *peroxide of manganese*, IODINE is liberated, which may be readily recognized by the violet color of its vapor. If concentrated sulphuric acid alone be used, sulphurous acid will be evolved with the iodine. Should the quantity of iodine present be very minute, the characteristic color of its vapor will not appear distinctly, and the operator will be obliged to resort to the use of starch : viz.

8. If to a solution of iodine, of hydriodic acid, or of an iodide—(in which latter case, the iodine is to be first liberated by addition of nitric acid)—thin *starch paste* be added, the fluid will acquire a more or less violet or blackish-blue tint, owing to the formation of IODIDE OF STARCH, even though only the most minute traces of iodine be present. Should the amount of iodine present be considerable, a blackish-blue precipitate of iodide of starch will be formed. If solutions of chlorine be used to effect the liberation of the iodine, this should be added very cautiously to prevent the formation of chloride of iodine, since no blue solution would appear in that case, chloride of iodine being a colorless substance. The best way of detecting the iodine in dry compounds of any description is, to introduce the compound under examination into a flask, to pour concentrated sulphuric acid over it, and to close the flask loosely with a stopper to which is attached a moistened slip of paper, or better still, white cotton cloth, covered with starch powder, or imbued with starch paste. After the lapse of a few hours this will acquire a blue tint, even though only a minute trace of iodine be present.

9. The iodides manifest with sulphuric acid in conjunction with chromate of potassa (compare § 101. *a.* 6.) the same deportment they exhibit with sulphuric acid alone.

d. HYDROCYANIC ACID. (Cy H).

1. Hydrocyanic acid is a colorless, volatile, inflammable liquid, the odor of which resembles that of bitter almonds ; it is miscible with water in all proportions, and speedily undergoes spontaneous decomposition when in its pure state.

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2. Those cyanides which have an alkali or alkaline earth for base, are soluble in water. They are readily decomposed by acids, even by carbonic acid, but ignition fails to decompose them when the access of air is precluded. When fused with oxides of lead, copper, antimony, tin, &c., the cyanides reduce these oxides, and are converted into cyanates. Only a few of those cyanides which contain heavy metals are soluble in water; all of them are decomposed upon ignition, and resolved either into cyanogen gas, and metal, such are the cyanides of the noble metals; or into nitrogen gas and carburets, such are the cyanides of the other heavy metals. Many of the cyanides with heavy metals are not decomposed by dilute oxygen acids, and .but with difficulty by concentrated nitric acid. Hydrochloric acid and sulphuretted hydrogen decompose most of them readily and completely.—Cyanogen combines with several metals, (iron, manganese, cobalt, chromium,) forming compound radicals, in which many of the usual reactions fail to detect the presence of the metals.

3. *Nitrate of silver* produces, in solution of free hydrocyanic acid and alkaline cyanides, white precipitates of CYANIDE OF SILVER, (Ag Cy), which are readily soluble in cyanide of potassium, dissolve with some difficulty in ammonia, and are insoluble in nitric acid; these precipitates are decomposed upon ignition, and leave metallic silver with some paracyanide of silver.

4. The addition of a solution of *protosulphate of iron* which has been for some time in contact with the air, to a solution of an alkaline cyanide, gives rise to the formation of ferrocyanide of potassium, which remains in solution, and, from the removal of the free alkali, of hydrated ferroso-ferric oxide, which precipitates. If hydrochloric acid be now added in excess, this precipitate will redissolve, and a new precipitate of PRUSSIAN BLUE will be formed, or the fluid will at least acquire a blue tint. (Compare § 89. *f.* ð). Free hydrocyanic acid must consequently first be combined with an alkali before its detection by this method can be attempted.

5. If to a solution of hydrocyanic acid, potassa be added in excess, and subsequently finely powdered *peroxide of mercury,* the latter substance will as readily dissolve as it would in free hydrocyanic acid. Since peroxide of mercury is soluble in

alkaline fluids *only in presence of hydrocyanic acid*, this reaction may be looked upon as a positive test for hydrocyanic acid.

6. On mixing a liquid containing hydrocyanic acid, with a small quantity (one or two drops) of yellow hydrosulphuret of ammonium and a trace of ammonia, and then warming in a porcelain dish until the mixture becomes colorless, sulphocyanide of ammonium is formed, which becomes of a deep blood red on the addition of a persalt of iron. (Liebig). This reaction is exceedingly delicate. The following formula expresses the transformation of hydrocyanic acid into sulphocyanide of ammonium.
$$N\ H_4\ S_5 + 2\ (N\ H_4\ O) + 2\ Cy\ H = 2\ (Cy\ S_2 + N\ H_4) + N\ H_4\ S + 2\ H\ O.$$

7. Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. The following process is pursued to detect the radical in this compound. The solution under examination is mixed with hydrochloric acid and metallic iron. This gives rise to the separation of metallic mercury, and formation of hydrocyanic acid and protochloride of iron, (which latter changes partially to perchloride in the air). If potassa be now added to the fluid, ferrocyanide of potassium and ferroso-ferric oxide will be formed, and finally, upon supersaturation with hydrochloric acid, Prussian blue. Cyanide of mercury may also be readily decomposed by sulphuretted hydrogen, with which it forms sulphurets of mercury and hydrocyanic acid. The action of heat, as already stated at 2. decomposes the cyanide of mercury into metallic mercury and cyanogen gas, which latter may be readily recognized by the characteristic effect which it produces upon the olfactory organs, and moreover by the crimson tint of its flame.

8. In the ferro and ferri-cyanides with alkaline bases, the ferro and ferri-cyanogen may be readily detected, the former by means of *solution of a persalt of iron*, or *solution of a proto-salt of copper*, and the latter by means of solution of *proto-salt of iron*. The distillation of these double cyanides with sulphuric acid gives rise to the evolution of free hydrocyanic acid. The insoluble ferrocyanides and ferricyanides undergo decomposition, when heated with caustic potassa, or with carbonate of potassa; ferrocyanide

of potassium is formed, and the metals separate as pure oxides, or as carbonates.

e. HYDROSULPHURIC ACID. (H S).

Sulphuretted Hydrogen Gas.

1. Sulphuretted hydrogen, at the common temperature and under common atmospheric pressure, is a colorless, inflammable gas, soluble in water, and which may be readily recognized by its characteristic smell of rotten eggs.

2. The alkaline sulphurets, or those of the alkaline earths, are alone soluble in water. These, and the sulphurets of metals of the fourth group, such as the sulphurets of iron and manganese for instance, are decomposed by dilute mineral acids, with evolution of sulphuretted hydrogen gas, which may be readily detected by its peculiar smell, and by its action upon solution of lead. (Vide 3). The decomposition of higher sulphurets is attended also with separation of sulphur in a highly divided state ; this sulphur precipitate may be readily distinguished from similar precipitates by its inflammability. Part of the sulphurets of the fifth and sixth group are decomposed by concentrated and boiling hydrochloric acid, with evolution of sulphuretted hydrogen gas, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury resist the action of both hydrochloric and nitric acids, but dissolve readily in aqua regia. Upon the solution of sulphurets in nitric acid, and in aqua regia, sulphuric acid is formed, and the process of solution is, moreover attended, in most cases, with separation of sulphur which is readily recognized by its color, and by its deportment upon heating.

3. When sulphuretted hydrogen in solution, or in the gaseous form, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates of SULPHURET OF SILVER or SULPHURET OF LEAD are formed. (Vide § 91. *a.* and § 91. *c.*) In cases, therefore, where the mere smell fails to afford sufficient proof of the presence of sulphuretted hydrogen, these reagents will lead to positive conviction. When the sulphuretted hydrogen is present

in the gaseous form, a small slip of paper, moistened with solution of basic acetate of lead, is to be placed in the air which it is intended to test for the presence of this gas; if sulphuretted hydrogen be present, this paper will become covered with a thin, brownish-black and lustrous film of sulphuret of lead.

4. When sulphurets are exposed to the *oxidizing flame of the blow-pipe,* the sulphur burns with a blue flame, emitting at the same time the well-known odor of sulphurous acid.

5. On heating a finely-powdered metallic sulphuret in a porcelain dish with solution of potassa until the potassa begins to fuse, or by fusing the portion to be tested, in a platina spoon with hydrate of potassa, then dissolving in a little water and bringing the solution in contact with a piece of bright silver, (a new silver coin answers this purpose,) the metal on warming, will become of a blackish-brown color from the formation of sulphuret of silver; by rubbing the silver with leather and carbonate of lime it may again be polished. (Kobell.)

Recapitulation and remarks.—Most of the acids of the first group are also precipitated by nitrate of silver, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, since the former are *soluble* in dilute nitric acid, whilst the latter are *insoluble* in that menstruum. The presence of hydrosulphuric acid interferes more or less with the testing for the other acids of the second group; this acid must, therefore, if present, be removed first, before we can proceed to test for the other acids. The removal of the hydrosulphuric acid, when present in the free state, may be effected by simple ebullition, and when present in the form of an alkaline sulphuret by the addition of a metallic salt, such as will not precipitate any of the other acids, or at least will not precipitate them from acid solutions. Hydriodic and hydrocyanic acids may be detected even in presence of hydrochloric or hydrobromic acid, by the equally characteristic and delicate reactions with starch and with solution of ferroso-ferric oxide. But the detection of chlorine and bromine is more or less difficult in presence of iodine and cyanogen. Should these latter substances be present, it will

be necessary therefore to remove them before proceeding to test for chlorine and bromine. The separation of the cyanogen may be readily effected by converting the whole of the radicals present into salts of silver, and igniting the mixed compound produced, when the cyanide of silver will undergo decomposition, whilst the chloride, bromide, and iodide of silver will remain unaltered. The iodine may now be separated from the chlorine and bromine, by treating the mixed silver compound with ammonia, since the iodide of silver is nearly insoluble in that menstruum. A still more accurate separation may be effected by precipitating the iodine as protiodide of copper, since the whole of the chlorine and bromine remains in solution in this process. Bromine is to be detected by the side of chlorine, by adding to the mixed compound under examination, solution of chlorine, or hydrochloric acid and chloride of lime, and dissolving the liberated bromine with ether. Chlorine by the side of bromine may be detected by the reaction which it manifests with chromate of potassa and sulphuric acid.

Third Group of the inorganic Acids.

ACIDS WHICH ARE NOT PRECIPITATED BY SALTS OF BARYTA NOR BY SALTS OF SILVER: *Nitric Acid—Chloric Acid.*

§ 102.

a. NITRIC ACID. (NO_5).

1. The anhydrous nitric acid crystallizes in six-sided prisms, they melt at 85° Fahr., and boil at 113° Fahr. (Deville, Compt. Rendus, xxviii. 257). The hydrate of pure nitric acid is a colorless, exceedingly caustic fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors nitrogenous matter intensely yellow. Admixture of nitrous acid imparts to hydrated nitric acid a red color.

2. All the neutral salts of nitric acid are soluble in water; only a few of the basic nitrates are insoluble in this menstruum. All nitrates without exception undergo decomposition at an intense red heat. Those with alkaline bases yield oxygen and nitrogen; the rest yield oxygen and nitrous or hyponitric acid.

3. When a nitrate is thrown upon *red-hot charcoal,* or when charcoal or some organic substance, paper for instance, is brought into contact with a nitrate in fusion, DEFLAGRATION takes place, i. e. the charcoal burns at the expense of the oxygen of the nitric acid, the combustion being attended with vivid scintillation.

4. If the mixture of a nitrate with *cyanide of potassium* in powder be heated on a platinum plate, a vivid DEFLAGRATION will ensue, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected by this reaction.

5. If the solution of a nitrate be mixed with one-fourth part of its quantity of concentrated sulphuric acid, and a crystal of *protosulphate of iron* thrown into the cooled mixture, the fluid immediately surrounding this crystal will acquire a DARK BROWN COLOR, which will generally disappear upon simple agitation of the fluid, and invariably upon the application of heat. In this process, the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combines with the protoxide, and converts a portion of it into peroxide, and the remaining nitric oxide combines with the remaining portion of the protoxide of iron, forming a peculiar soluble compound, which, upon its solution in the water of the menstruum, imparts a brownish black color to the latter.

6. If to the solution of a nitrate some sulphuric acid be added, and as much *solution of indigo* in sulphuric acid as will impart a faint light-blue tint to the fluid, and the mixture be heated to boiling, the blue coloration of the fluid will change to a faint yellowish tint, or the solution will even become perfectly colorless. This change of color is owing to the oxidation of the indigo at the expense of the oxygen of the nitric acid which is liberated by the sulphuric acid. It must be borne in mind, however, that several other substances besides nitric acid, cause decoloration of solution of indigo—free chlorine particularly produces this effect.

7. If concentrated sulphuric acid be poured over the mixture of a nitrate with *copper-filings,* in a test-tube, the air in the latter will acquire a yellowish-red tint, owing to the nitric oxide gas which is liberated upon the oxidation of the copper by the nitric acid, combining with the oxygen of the air and forming nitrous

acid. This coloration may be observed most distinctly by looking through the tube in the direction of its length.

b. CHLORIC ACID. (Cl O₅).

1. Chloric acid forms in its most highly concentrated solution a yellow oily fluid the odor of which resembles that of nitric acid. It first reddens litmus and afterwards bleaches it. Dilute chloric acid is colorless and inodorous.

2. All chlorates are soluble in water. When chlorates are heated to redness, the whole of their oxygen escapes and metallic chlorides remain.

3. When heated with *charcoal* or some organic substance, the chlorates DEFLAGRATE, and this with far greater violence than the nitrates.

4. When the mixture of a chlorate with *cyanide of potassium is* heated on a platinum plate, DEFLAGRATION takes place, attended with strong detonation and ignition, even though the chlorate be present only in very small quantity. (This experiment should be made with minute quantities only).

5. Free chloric acid oxidizes and decolors *indigo* in the same manner as nitric acid ; consequently if the solution of a chlorate be mixed with sulphuric acid and solution of indigo, and the mixture be heated to boiling, the same phenomena will manifest themselves which we have described while treating of nitric acid, (vide *a. 6*).

6. If the solution of a chlorate be colored light blue with a small amount of *solution of indigo* in sulphuric acid, and a solution of *sulphurous acid* in water be dropped cautiously into the blue fluid, the color of the indigo will disappear. The cause of this equally characteristic and delicate reaction is, the sulphurous acid deprives the chloric acid of its oxygen, and the thus liberated chlorine decolors the indigo.

7. Upon heating chlorates with *hydrochloric acid,* the constituents of the two acids decompose, forming water and bichlorate of chlorous acid (2 Cl O₅, Cl O₃).

8. *Concentrated sulphuric acid,* when poured over a chlorate, causes the conversion of two-thirds of the metallic oxide into a

sulphate and the remaining one-third into a hyperchlorate; this conversion is attended, moreover, with liberation of chlorate of chlorous acid, which imparts an intensely yellow tint to the sulphuric acid, and manifests its presence by its odor and the greenish color of the evolved gas. [3 $(KO, Cl O_5)$ + 4 SO_3 = 2 $(KO, 2 SO_3)$ + $KO, Cl O_7$ + $(Cl O_5 + Cl O_3)$]. The application of heat must be avoided in this experiment, and the quantities operated upon should be very minute, since otherwise the decomposition might ensue with such force and energy as to cause an explosion.

Recapitulation and remarks.—Of all the reactions which have been suggested to effect the detection of nitric acid, those with proto-sulphate of iron and sulphuric acid, and with copper filings and sulphuric acid, yield the most positive results; with regard to deflagration with charcoal, detonation with cyanide of potassium, and decoloration of solution of indigo, we have seen that these reactions belong equally to chlorates as to nitrates, and are consequently decisive only when no chloric acid is present. The best way to ascertain whether chloric acid be present or not, is to ignite the sample under examination, dissolve the mass, and test the solution with nitrate of silver. Should a chlorate be present, this will be converted into a chloride upon the ignition of the sample, and nitrate of silver will now precipitate chloride of silver from the solution. However, this test is thus simple only when no chloride happens to be present with the chlorate. But should the substance under examination contain an admixture of chloride, it will be necessary, in the first place, to add nitrate of silver to its solution, until this ceases to produce a precipitate; the fluid is then to be filtered off from the latter, the filtrate evaporated and the residue ignited. It is, however, generally unnecessary to pursue this circuitous way, since the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid.

II. ORGANIC ACIDS.

First Group.

ACIDS WHICH ARE PRECIPITATED BY CHLORIDE OF CALCIUM, UNDER CERTAIN CONDITIONS : *Oxalic Acid—Tartaric Acid— Paratartaric or Racemic Acid—Citric Acid—Malic Acid.*

§ 103.

None of these acids volatilize without suffering decomposition.

a. OXALIC ACID.

For the reactions of oxalic acid I refer to § 99, *c.*

b. TARTARIC ACID. *   ($C_4 H_2 O_5 = \overline{T}$).

1. Tartaric acid forms colorless crystals of an agreeable acid taste, which are persistent in the air, and soluble in water and in spirit of wine. Tartaric acid when heated fuses at first, and afterwards becomes carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar.

2. The tartrates with alkaline bases are soluble in water, and so are those with the metallic oxides of the third and fourth group; those of the tartrates which are insoluble in water, dissolve in hydrochloric or nitric acid. The tartrates suffer decomposition when heated to redness ; charcoal separates and the same peculiar odor is emitted as attends the carbonization of free tartaric acid.

3. If to a solution of tartaric acid, or to that of a tartrate, solution of *peroxide of iron,* of *protoxide of manganese* or of *alumina* be added, and subsequently ammonia or potassa, no precipitation of peroxide of iron, of protoxide of manganese or of alumina will ensue, since the newly-formed double tartrates are not decomposed by alkalies. Tartaric acid prevents the precipitation of several other oxides by alkalies.

4. Free tartaric acid yields with *salts of potassa,* and more

* It will be observed, that some of the formulæ for the organic acids differ from those in use in English works ; but as this does not affect the results, it has been deemed best to adhere to the German text.

particularly with the acetate, a sparingly soluble precipitate of BITARTRATE OF POTASSA. A similar precipitate is formed, when acetate of potassa and free acetic acid, or bisulphate of potassa, are added to the solution of a neutral tartrate. When using bisulphate of potassa, addition in excess is to be most carefully avoided. The acid tartrate of potassa dissolves readily in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. The precipitation of the bitartrate of potassa may be greatly promoted by brisk agitation.

5. *Chloride of calcium* throws down from the solutions of neutral tartrates, a white precipitate of TARTRATE OF LIME $(Ca\,O,\overline{T})$. Presence of ammoniacal salts retards the formation of this precipitate for a more or less considerable space of time. Agitation of the fluid, or friction on the sides of the vessel, promotes the separation of the precipitate. Tartrate of lime dissolves in a cold solution of caustic potassa to a clear fluid. But upon boiling this solution, the dissolved tartrate of lime separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime-water* produces in solutions of neutral tartrates, or even in solutions of free tartaric acid, (if added till an alkaline reaction becomes manifest,) a white precipitate which dissolves readily in tartaric acid, and also in solution of sal ammoniac; after the lapse of several hours, the tartrate of lime separates again from the solution in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of sulphate of lime* fails to produce a precipitate in a solution of tartaric acid; whilst with neutral tartrates, this reagent produces a minute precipitate, after the lapse of some time.

c. PARATARTARIC ACID. (RACEMIC ACID). $C_4\,H_2\,O_5=\overline{R})$.

1. Racemic acid has the same composition as tartaric acid. In its crystallized state it contains two equivalents of water, of which it loses one at 212°. The crystals effloresce very slowly in dry air. Its deportment with solvents, and when acted upon by heat, is analogous to that which tartaric acid exhibits under the same circumstances.

N 2

2. The deportment and properties of the paratartrates are very similar to those of the corresponding tartrates. Many of them differ, however, in form, solubility, and proportional amount of water. The paratartrates, like the tartrates, prevent the precipitation of alumina, protoxide of manganese, peroxide of iron, &c., by alkalies.

3. *Chloride of calcium* precipitates both from the solutions of free paratartaric acid and of paratartrates, PARATARTRATE OF LIME, (Ca O, $\overline{R}$), as a dazzling white powder. This precipitate is insoluble in sal ammoniac, but it dissolves completely in cold concentrated solution of potassa, and partially in dilute solution of potassa; this solution becomes turbid and gelatinous upon boiling, and clears again upon cooling.

4. *Lime-water* produces immediately, in solutions of neutral paratartrates, a white precipitate of PARATARTRATE OF LIME. It produces a similar precipitate in solution of free paratartaric acid, if added to alkaline reaction; but if a less amount of lime-water be used, so as to leave the solution still acid, the precipitate will form only after the lapse of a few moments. Paratartrate of lime is insoluble both in paratartaric and tartaric acids; it dissolves in hydrochloric acid, and upon addition of ammonia in excess, it precipitates again from this solution instantaneously, or after a few moments.

5. *Solution of sulphate of lime* produces immediately in solutions of neutral paratartrates a precipitate of paratartrate of lime; but from solutions of free paratartaric acid, this precipitate separates only after the lapse of from ten to fifteen minutes.

6. If crystallized paratartaric acid, or a paratratrate be heated with *concentrated sulphuric acid*, the latter will acquire a black color, and sulphurous acid and carbonic oxide gas will be evolved. Tartaric acid presents the same deportment.

d. CITRIC ACID. $(C_4 H_2 O_4 = \overline{Ci})$.

1. Citric acid crystallizes in colorless, pellucid, and inodorous crystals of an agreeable acid taste, and which, according to the circumstances attendant upon its formation, contain, besides one

equivalent of hydration water, a variable amount of water of crystalli-
zation.   Citric acid is unalterable in the air, and dissolves readily
in water and in alcohol.   When subjected to the action of heat,
citric acid fuses at first, and afterwards carbonizes, with emission
of pungent acid fumes, the odor of which may be readily distin-
guished from that emitted by tartaric acid upon carbonization.

2. The citrates with alkaline bases are readily soluble in water,
both in the neutral and acid state ; the same applies to the com-
pounds of citric acid with such of the metallic oxides as are weak
bases, with peroxide of iron, for instance.   Citrates, like tartrates,
and for the same reason, prevent the precipitation of peroxide of
iron, protoxide of manganese, alumina, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solution
of free citric acid, even upon boiling; but a precipitate of NEUTRAL
CITRATE OF LIME (Ca O, $\overline{C}$i) will immediately form if the free
citric acid be saturated with potassa or soda.   This precipitate is
insoluble in potassa, but it dissolves readily in solution of sal
ammoniac; upon boiling this solution, neutral citrate of lime
separates again in the form of a white crystalline precipitate.   If
a solution of citric acid, containing an admixture of chloride of
calcium, be saturated with ammonia, no precipitation will ensue in
the cold, but upon boiling the clear fluid, neutral citrate of lime
will suddenly precipitate.

4. *Lime-water* produces no precipitate in cold solutions of
citric acid or of citrates.   But upon heating the solution to boiling,
with a tolerable excess of hot lime-water, a white precipitate of
CITRATE OF LIME is formed, of which the greater portion redis-
solves upon cooling, simply because it is less soluble in hot than
in cold water.

5. *Acetate of lead,* when added in excess, produces in solutions
of citric acid, a white precipitate of CITRATE OF LEAD, (Pb O, $\overline{C}$i),
which is very sparingly soluble in ammonia, but dissolves readily
in citrate of ammonia.   The addition of citric acid in excess to
solution of neutral acetate of lead also gives rise to the forma-
tion of a precipitate of citrate of lead; but this precipitate redis-
solves readily upon the addition of ammonia.   We have just now
seen that the citrate of lead is but very sparingly soluble in am-

monia; the solution therefore is caused here by the citrate of ammonia, which the excess of the acid forms with the ammonia added.

6. Upon subjecting citric acid or citrates with concentrated sulphuric acid to the action of heat, carbonic oxide and carbonic acid escape at first, the sulphuric acid retaining its natural appearance; upon continued ebullition, however, the solution acquires a dark color, and sulphurous acid is evolved.

$$e. \text{ MALIC ACID. } (C_4 \ H_2 \ O_4 = \overline{M})$$

1. Malic acid crystallizes with difficulty, forming crystalline crusts, which deliquesce in the air, and dissolve readily in water and in alcohol. Malic acid, when exposed to a temperature of 892°, is resolved into MALEIC ACID, $(C_4 \ H \ O_3)$, and FUMARIC ACID $(C_4 \ H \ O \ )$. This deportment of malic acid is highly characteristic. When the experiment is made in a small spoon, pungent acid vapors of maleic acid are evolved with effervescence. If the experiment be conducted in a small tube, these fumes will condense forming crystals in the colder part of the tube. The fumaric acid remains as a residue.

2. Malic acid forms with most bases, salts which are soluble in water. The acid malate of potassa dissolves in water. Malic acid prevents, like tartaric acid, the precipitation of peroxide of iron by alkalies.

3. *Chloride of calcium* fails to produce a precipitate both in solutions of free malic acid, and of malates. But if, after the addition of the chloride of calcium, alcohol be added to the solution of a malate, MALATE OF LIME $(Ca \ O, \overline{M})$ will immediately separate in the form of a white powder.

4. *Lime-water* produces no precipitate, either in solutions of free malic acid, or in solutions of malates.

5. *Acetate of lead* throws down from solutions of malic acid and of malates, a white precipitate of MALATE OF LEAD $(Pb \ O, M)$. The most distinguishing mark of this precipitate is the lowness of its fusing point; it melts at a temperature below the boiling point of water, and fuses accordingly when the fluid wherein it is suspended is heated to ebullition; the fused mass resembles resin

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which has been melted under water. This reaction is distinctly marked only when the malate of lead is tolerably pure; admixture of other salts of lead impairs it, or even prevents it altogether.

6. Upon subjecting malic acid, with concentrated sulphuric acid, to the action of heat, the sulphuric acid acquires a black color, and sulphurous acid is evolved.

Recapitulation and remarks.—Of the organic acids of this group, the tartaric acid and paratartaric acid are sufficiently characterized by the sparing solubility of their acid potassa salts, by the deportment of their lime salts with solution of potassa, and by the peculiar odor which they emit upon carbonization. Tartrate of lime is soluble both in free tartaric acid and chloride of ammonium; whilst the paratartrate of lime is insoluble in these substances. This different deportment of the respective lime salts of the two acids, affords an excellent means of distinguishing the latter from the former.—(It must be borne in mind, that tartrate of lime separates again from its solution in chloride of ammonium, after a shorter or longer space of time, according to the greater or less degree of concentration of the solution.)—Paratartaric acid differs from tartaric acid, moreover, in its deportment with solution of sulphate of lime. The behaviour of paratartaric acid with solution of sulphate of lime, is similar to that which oxalic acid manifests with this reagent. When operating upon the free acids, however, this similarity of deportment is not very liable to occasion mistakes, since the precipitate which solution of sulphate of lime produces in solutions of paratartaric acid, never separates instantaneously. The oxalates, moreover, are to be readily distinguished from the paratartrates by the deportment which they present when exposed to the action of heat as well as with sulphuric acid.

Citric acid is recognized most safely and positively by its behaviour with lime-water, or with chloride of calcium and ammonia; the sparing solubility of the washed citrate of lead in ammonia, distinguishes citric acid from tartaric and paratartaric acids. The other reagents which produce precipitates or other alterations in the solutions of citric acid and citrates, such as per-

chloride of gold, and the salts of silver and mercury, &c., present the same or a similar deportment with tartaric and paratartaric acids, and therefore, will not enable us to distinguish between these acids. Malic acid would be sufficiently characterized by the fusion of malate of lead upon boiling with water, were this reaction more delicate, and not so readily impaired or prevented by the presence of other acids. The formation of a precipitate upon the addition of alcohol to the mixture of a supposed solution of free malic acid, or a malate with chloride of calcium, is to be looked upon as an indication of the presence of malic acid only when the absence of all other acids of which the lime salts are sparingly soluble in water, and altogether insoluble in alcohol, (e. g. sulphuric acid, boracic acid,) is most clearly demonstrated. *At all events, the precipitate produced upon the addition of alcohol, must be subjected to further examination before it can be with certainty pronounced to consist of malate of lime.* The most positive results are attained by heating the pure malic acid in a glass tube; but this test is not applicable under all circumstances.

Second Group of the Organic Acids.

ACIDS, WHICH CHLORIDE OF CALCIUM FAILS TO PRECIPITATE UNDER ANY CIRCUMSTANCES, BUT WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY PERCHLORIDE OF IRON: *Succinic acid—Benzoic acid.*

§ 104.

a. SUCCINIC ACID. $(C_4 \ H_2 \ O_3 = \overline{S})$.

1. Succinic acid forms colorless and inodorous crystalline scales or prisms, of feebly acid taste, which are soluble in water, alcohol, and ether, and volatilize without residue when exposed to the action of heat. The officinal acid has an empyreumatic odor, and leaves a small carbonaceous residue, upon volatilization.

2. The succinates are decomposed at a red heat, with the exception of succinate of ammonia; those which have an alkali or alkaline earth for base, are converted into carbonates in this process. Most of the succinates are soluble in water.

3. *Perchloride of iron* produces in solutions of neutral suc-
cinates of the alkalies, brownish, or pale red, bulky precipitates of
PERSUCCINATE OF IRON (Fe$_2$ O$_3$, $\overline{S}_2$). Persuccinate of iron dis-
solves readily in acids; ammonia decomposes it, causing the sepa-
ration of a less bulky precipitate of a basic persuccinate of iron,
and combining with the greater portion of the acid, forms succi-
nate of ammonia which dissolves.

4. *Acetate of lead* yields with succinic acid a white precipitate
of neutral SUCCINATE OF LEAD (Pb O, $\overline{S}$) which is soluble in an
excess of succinic acid, in solution of acetate of lead, in nitric
acid, and also, although less readily, in acetic acid. When acted
upon by ammonia the neutral succinate of lead is converted into a
basic salt (3 Pb O, $\overline{S}$).

5. A mixture of *alcohol, ammonia*, and *solution of chloride of
barium*, produces in solutions of free succinic acid and of succi-
nates, a white precipitate of SUCCINATE OF BARYTA (Ba O, $\overline{S}$).

6. *Pernitrate of mercury* and *nitrate of silver* also precipitate
the succinates; the precipitates, however, are not possessed of any
characteristic properties.

b. BENZOIC ACID.   (C$_{14}$ H$_5$ O$_3$=Bz O).

1. Pure benzoic acid appears in the form of white scales or
needles, or simply as a crystalline powder. It volatilizes com-
pletely when heated. The fumes of benzoic acid cause a peculiar
irritating sensation in the throat, and provoke coughing. The
common officinal benzoic acid has the odor of benzoin, and leaves
a small carbonaceous residue upon volatilization. Benzoic acid is
very sparingly soluble in cold water, but it dissolves without diffi-
culty in hot water, and in alcohol.

2. Most of the benzoates are soluble in water; only those with
weak bases, such, for instance, as peroxide of iron are insoluble.
The soluble benzoates have a peculiar irritating taste. The addi-
tion of a *strong acid* to aqueous solutions of benzoates displaces
the benzoic acid, which separates in the form of a dazzling white,
sparingly soluble powder. Benzoic acid is also expelled from the
insoluble benzoates by such strong acids as form soluble salts with
the bases with which the benzoic acid is combined.

3. Benzoic acid comports itself with *perchloride of iron* like succinic acid. The PERBENZOATE OF IRON, ($Fe_2 O_3$, 3 Bz O), however, is of a far lighter and more yellow color than the persuccinate. It is decomposed by ammonia in the same manner as the latter.

4. *Acetate of lead* fails to precipitate free benzoic acid, and benzoate of ammonia, at least immediately ; but it produces white flocculent precipitates in solutions of benzoates with fixed alkaline bases.

5. A mixture of *alcohol, ammonia,* and *solution of chloride of barium* produces NO precipitate either in a solution of free benzoic acid, or in solutions of the alkaline benzoates.

Recapitulation and remarks.—Succinic and benzoic acids are distinguished from all other acids by their ready volatility and their behaviour with perchloride of iron. They differ from one another in the color of their persalts of iron in their respective deportments with chloride of barium and alcohol, but principally in their different degrees of solubility, succinic acid being readily soluble, whilst benzoic acid is very difficult of solution. Succinic acid is seldom perfectly pure, and may therefore be generally detected by the odor of oil of amber which it emits.

The following method will serve to effect the respective detection of benzoic and succinic acid when present side by side : the solution of the compound under examination, is precipitated with perchloride of iron, the precipitate formed is heated with ammonia, and the solution thus obtained filtered. The filtrate is then concentrated by evaporation, one portion of it mixed with hydrochloric acid, the other with chloride of barium and alcohol.

Third Group of the Organic Acids.

ACIDS WHICH ARE NOT PRECIPITATED, UNDER ANY CONDITION, EITHER BY CHLORIDE OF CALCIUM OR BY PERCHLORIDE OF IRON : *Acetic acid—Formic acid.*

§ 105.

a. ACETIC ACID. $(C_4 H_3 O_3 = \bar{A})$.

1. The hydrate of acetic acid forms transparent crystalline scales which fuse at 68° to a colorless fluid of a peculiar pungent odor, and exceedingly acid taste. When exposed to the action of heat, it volatilizes completely, forming pungent vapors which burn with a blue flame. It is miscible with water in all proportions ; it is to such mixtures of the acid with water that the name of acetic acid is commonly applied. The hydrate of acetic acid is also soluble in alcohol.

2. The acetates undergo decomposition at a red-heat; among the products of this decomposition, we generally find acetic acid, and invariably acetone. The acetates of the alkalies and alkaline earths are converted into carbonates, in this process ; whilst many of those with metallic bases leave the metal behind in its pure state, others in the form of oxide. The residues which the acetates leave upon ignition are all carbonaceous. Nearly the whole of the acetates dissolve in water and in alcohol; most of them are readily soluble in water, a few only are difficult of solution in this menstruum.

3. If *perchloride of iron* be added to acetic acid, and the acid be then saturated with ammonia, or if a neutral acetate be mixed with perchloride of iron, the solution will acquire a dark red color, owing to the formation of PERACETATE OF IRON. Ammonia precipitates the whole of the peroxide of iron from this solution.

4. Neutral acetates (but not free acetic acid) yield with *nitrate of silver,* white crystalline precipitates of ACETATE OF SILVER, $(Ag O, \bar{A})$, which are very sparingly soluble in cold water. They dissolve more easily in hot water, but separate again, upon cooling, in the form of very fine crystals. Ammonia dissolves them readily ; free acetic acid does not increase their solubility in water.

5. Protonitrate of mercury produces in solutions of acetic acid, and more readily still in solutions of acetates, white scaly crystalline precipitates of PROTACETATE OF MERCURY, (Hg$_2$ O, $\overline{A}$), which are sparingly soluble in water and acetic acid in the cold, but dissolve without difficulty in an excess of the precipitant. Protacetate of mercury dissolves in water upon the application of heat, but separates again upon cooling, in the form of small crystals; in this process, the salt undergoes partial decomposition, a portion of the mercury separates in the metallic state, and imparts a grey color to the precipitate. When the protacetate of mercury is boiled with dilute acetic acid instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. When acetates are heated with *dilute sulphuric acid*, ACETIC ACID is evolved, and may be detected by its pungent odor. But when the acetates are heated with a mixture of equal portions of *concentrated sulphuric acid* and *alcohol*, ACETIC ETHER (C$_4$ H$_5$ O, $\overline{A}$ =Ae O, $\overline{A}$) is formed. The odor of this ether is highly characteristic and agreeable; it is most perceptible upon agitating the mixture when somewhat cooled, and is less liable to lead to mistakes than the pungent odor of the free acetic acid.

7. If acetates be distilled with dilute sulphuric acid, and the distillate digested with an excess of oxide of lead, part of the latter will dissolve as a basic acetate of lead, which may be readily detected by its alkaline reaction.

b. FORMIC ACID.   (C$_2$ H O$_3$=Fo O$_3$).

1. The hydrate of formic acid is a colorless, pellucid, slightly fuming liquid, of a characteristic and exceedingly penetrating odor. When cooled to below 32°, it crystallizes in colorless plates. It is miscible in all proportions with water and with alcohol. When exposed to the action of heat, it volatilizes completely, and burns with a blue flame.

2. The formiates, like the corresponding acetates, leave upon ignition, either carbonates, oxides, or metals behind, the process being attended with separation of charcoal, and evolution of carburetted hydrogen, carbonic acid, and water. All the compounds of formic acids with bases are soluble in water; alcohol likewise dissolves some of them.

3. Formic acid presents the same deportment with *perchloride of iron* as acetic acid.

4. *Nitrate of silver* fails to precipitate free formic acid, and decomposes the alkaline formiates only in concentrated solutions. The white, sparingly soluble, crystalline precipitate of FORMIATE OF SILVER, (Ag O, Fo O$_3$), acquires very rapidly a deeper tint, owing to the separation of metallic silver. This reduction of the oxide of silver to the metallic state takes place even in the cold, after the lapse of some time, and immediately, upon applying heat to the fluid containing the precipitated formiate of silver. The same reduction of the oxide of silver to the metallic state is observed in solutions of free formic acid and of formiates even when so dilute, that the addition of the nitrate of silver fails to produce a precipitate. The rationale of this reduction is as follows: the formic acid, which may be looked upon as a compound of carbonic oxide with water, deprives the oxide of silver of its oxygen, thus causing the formation of carbonic acid which escapes, and of water, whilst the reduced silver separates in the metallic state.

5. *Protonitrate of mercury* gives no precipitate with free formic acid; but in concentrated solutions of alkaline formiates, this reagent produces a white, sparingly soluble precipitate of PROTOFORMIATE OF MERCURY, (Hg$_2$ O, Fo O$_3$), which rapidly becomes grey, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time but is immediate when heat is applied to the fluid containing the precipitate. This reduction is also attended with the formation of carbonic acid and water, and takes place both in solutions of free formic acid, and in fluids which are so highly dilute that the protoformiate of mercury is retained in solution, instead of precipitating.

6. If formic acid or an alkaline formiate be heated from 140° to 158° with *perchloride of mercury*, PROTOCHLORIDE OF MERCURY will precipitate. If the mixture be heated to the boiling point of water, metallic mercury will separate with the protochloride.

7. When formic acid or a formiate is heated with *concen-*

trated sulphuric acid, the formic acid is resolved into water, and carbonic acid gas, which escapes with effervescence, and when kindled, burns with a blue flame. The mixture does not turn black in this process. The rationale of this decomposition of the formic acid is this : the sulphuric acid withdraws from the formic acid the water or the oxide necessary for the existence of the latter acid, and thus occasions a transposition of its elements (C_2 H O_3=2 C O+H O). Upon heating a formiate with dilute sulphuric acid, formic acid escapes, and may be readily detected by its odor. When a formiate is treated with a mixture of sulphuric acid and alcohol, formic ether is evolved, which is characterized by its peculiar arrack-like smell.

Recapitulation and remarks.—The reactions of acetic acid and formic acid are not so characteristic as those of many others; the positive detection of these two acids is accordingly to be based only upon the concurrence of all the various reactions which I have given. The odor of acetic acid and that of acetic ether form the most ready, its deportment with oxide of lead the most positive, test for acetic acid. Formic acid is best detected by its behaviour with sulphuric acid and with the salts of the noble metals. The separation of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of peroxide of mercury, or of oxide of silver. Formic acid reduces the oxides, and suffers decomposition, being resolved into carbonic oxide and water; whilst the acetic acid combines with them, forming acetates which remain in solution.

PART II.

SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.
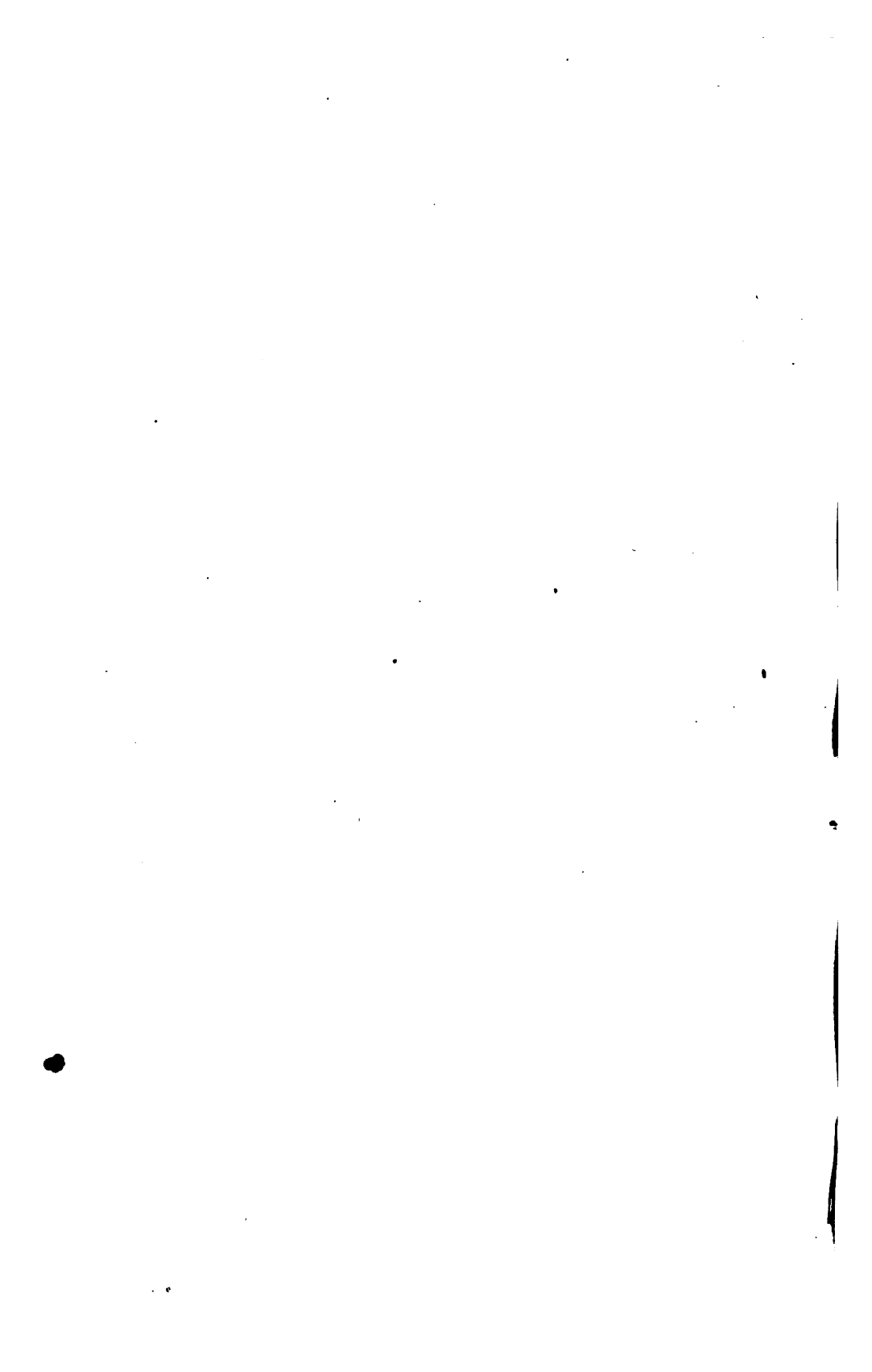
PART II.

PRELIMINARY REMARKS

ON THE

COURSE OF QUALITATIVE ANALYSIS IN GENERAL

AND ON THE

PLAN OF THIS PART OF THE PRESENT WORK IN PARTICULAR.

THE knowledge of reagents and of the deportment which other bodies exhibit with them, enables us to ascertain at once whether a compound of which the physical properties permit an inference as to its nature, is in reality what we suspect it to be. Thus, for instance, by a few simple reactions we prove whether a body which appears to be calcareous spar, is really carbonate of lime, and that another, which we deem gypsum, is sulphate of lime. This knowledge usually suffices to ascertain, whether a certain body is present or not in some compound or other; for instance, whether or not a powder contains protochloride of mercury. But if our design is to ascertain the chemical nature of a substance entirely unknown to us,—if we wish to discover *all* the constituents of a mixture or chemical compound,—if we intend to prove that, besides certain bodies which we have detected in a mixture or compound, no other substance can be present,—consequently, if a COMPLETE QUALITATIVE ANALYSIS is our object,

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the mere knowledge of the reagents, and of the reactions of other bodies with them, will not suffice for the attainment of this end ; this requires the additional knowledge of a systematic and progressive course of analysis, in other words, the knowledge of the *order*, and *succession* in which solvents, together with general and special reagents, ought to be applied both to effect the speedy, and safe detection of every individual component of a compound or mixture, and to prove with certainty the absence of all other substances. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method whatever in our investigations and experiments, analyzing becomes (at least in the hand of a novice) mere guess work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits, and at others total failures.

Every analytical investigation must therefore be based upon a definite method. But it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances, will, on the contrary, generally lead to the adoption of different methods for different cases. However, all analytical methods agree in this, that the substances present, or supposed to be present, in a compound or mixture, are in the first place to be classed into certain groups, which are then again to be subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order, and succession in which reagents are applied, and partly on their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a certain definite course, or system of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every imaginable case, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will, in certain given cases, most readily and rapidly lead to the attainment of the object in view.

The exposition of such a systematic course, adapted to all cases

tested by experience, and combining simplicity with the greatest possible security, is the object of the second part of this work.

The elements and compounds comprised ·in it are the same which I have enumerated in my preliminary remarks.

The construction of a universally applicable systematic course of analysis requires due regard to, and provision for, every contingency that may possibly arise; it is accordingly self-evident that the various substances treated of—(however mixed and intermixed with one another we may imagine them)—must be supposed free from extraneous organic matters, since the presence of such bodies prevents the manifestation of many reactions, and causes various modifications in others. I do not by any means intend to assert here that the proposed systematic course is inapplicable even in presence of many organic substances, especially of such as dissolve in water forming colorless or clear solutions. Experience and due reflection in every individual case will best instruct the young chemist how to act in cases where dark coloring or slimy matters happen to be present. For the most important rules, and the method in general, I refer to § 132.

This part of the work is divided into two sections; the first contains PRACTICAL INSTRUCTIONS IN ANALYSIS, wherein I have laid down a systematic course which, progressing step by step, must finally lead to the end in view. At first sight, many parts of it may perhaps be deemed rather prolix; I think, however, that it would have scarcely been possible to shorten it, except at the expense of that clearness, and perspicuity which are so indispensable to render a work of this description really useful to the student. I hope, moreover, that my readers will soon become convinced by experience that this prolixity, after all, does not prove any serious bar to the celerity with which the systematic course may be gone through, since I have invariably arranged the phenomena which may occur, into clearly characterised cases, so that the student, having to look simply and exclusively to the case under his consideration, and one number always referring to the other, may save himself the trouble of reading through those parts which do not bear upon the particular question engaging his attention.

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The subdivisions of this practical course are, 1. Preliminary examination ; 2. Solution ; 3. Actual examination ; 4. Confirmatory experiments.

The third subdivision (the ACTUAL EXAMINATION) is again subdivided into, 1. Examination of compounds in which but *one base* and *one acid* are assumed to be present; and, 2. Examination of mixtures, or compounds in which all the substances treated of in the present work are assumed to be present. With respect to the latter section, I have to remark that where the preliminary examination has not afforded the most positive conviction of the absence of certain groups of substances, the student cannot safely disregard any paragraph referred to, in consequence of the phenomena that manifest themselves. In cases where the intention is simply to test a compound, or mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular numbers which ought to be attended to.

The second section contains an EXPLANATION OF THE PRACTICAL PROCESS : an exposition of the principles whereon the separation, and of the causes on which the detection of substances depend; it contains, moreover, various additions to the first section. Students are strongly recommended to make themselves early and thoroughly acquainted with this part, which may be properly considered a key to the first section.

In the appendix I give, 1. A GENERAL PLAN OF THE ORDER AND SUCCESSION IN WHICH I WOULD RECOMMEND THE YOUNG STUDENT TO ANALYSE SUBSTANCES FOR PRACTICE ; 2. INSTRUCTIONS HOW TO ARRANGE THE RESULTS OF HIS INVESTIGATION IN THE MOST ADVANTAGEOUS MANNER ; and 3. A TABULAR ARRANGEMENT OF THE MORE FREQUENTLY OCCURRING FORMS AND COMPOUNDS OF THE SUBSTANCES ENUMERATED IN MY PRELIMINARY REMARKS, BASED MORE PARTICULARLY UPON THEIR RESPECTIVE DEGREE OF SOLUBILITY IN WATER AND ACIDS. The first is intended to serve the pupil as a guide in his efforts to acquire a sound and thorough knowledge of qualitative analysis; the second is intended to afford him a means of obtaining a clear view over the whole domain of the science ; and the third will certainly prove useful to many who are not yet quite conversant with the various degrees of solubility

of substances, particularly when required to determine the manner the acids, bases, &c., detected in the course of an analysis, were originally combined in the examined substance, or what particular acid, or acids cannot possibly exist with certain bases in aqueous or acid solutions.

In compliance with the expressed wishes of many parties, I have added to this edition a chapter treating of the REACTIONS OF THE MORE FREQUENTLY OCCURRING ALKALOIDS, and containing a well-tried method to effect their detection in the systematic course of analysis.

FIRST SECTION.

PRACTICAL PROCESS.

I. PRELIMINARY EXAMINATION.

§ 106.

1. The operator has, in the first place, to examine the physical properties — (color, shape, hardness, gravity, odor, &c.) — of the substance which he intends to analyse, since these will often enable him in some measure to infer the nature of the said substance. Before proceeding to the application of any chemical process, the operator should invariably consider how much of the substance to be analysed he has at command, since it is necessary, at this early period of the examination, to calculate the quantity which may be used in the preliminary investigation. A reasonable economy is in all cases advisable, though we may possess the substance in large quantities; and it must be laid down as a fixed rule, never to use at once the whole of what we possess of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments.

§ 107.

A. THE BODY UNDER EXAMINATION IS SOLID.

I. IT IS NEITHER A PURE METAL NOR AN ALLOY.

1. The substance is fit for examination if in powder or in* **2** minute crystals ; but when in larger crystals or in solid pieces, it is necessary in the first place to reduce a portion of it to powder, if possible.

2. The powder is heated in a small iron spoon, over a spirit- **3** lamp ; the resulting phenomena may lead to many positive or probable conclusions regarding the nature of the substance.

    a. THE SUBSTANCE REMAINS UNALTERED : absence of **4** organic substances, salts containing water, readily fusible matters, and volatile bodies.

    b. IT FUSES READILY AND RE-SOLIDIFIES WITH EXPUL- **5** SION OF AQUEOUS VAPOR : salts which contain water of crystallization. If the solidified residue fuses again upon the application of an increased heat, *c* must be had re-gard to.

    c. IT FUSES WITHOUT EXPULSION OF AQUEOUS VAPOR. **6** A small piece of paper is added to the melting mass ; if deflagration takes place, this indicates the presence of NI-TRATES, or also of the more rarely occurring CHLORATES.

    d. IT VOLATILIZES COMPLETELY OR PARTLY. In the first **7** case, no fixed bases are present; in the latter, the substance contains a volatile body in admixture.

    a. No odor is emitted. In this case we have to look more particularly for compounds of AMMONIA,MERCURY, and ARSENIC.

    β. An odor is emitted. Should it be that of sulphurous acid, SULPHUR is present ; whilst the smell of iodine, with violet vapors, denotes the presence of free IODINE. With equal certainty free BENZOIC ACID, and many other sub-stances, may be detected by their odor on volatilizing.

* The marginal numbers commenced here are totally independent of the courses of analysis, their only use being to facilitate the references so fre-quently occurring.

e. THE SUBSTANCE IS A WHITE POWDER, TURNING YEL- **8**
LOW UPON THE APPLICATION OF HEAT ; this indicates
OXIDE OF ZINC, OXIDE OF LEAD, OR OXIDE OF BISMUTH ;
the oxide of zinc resumes its white color upon cooling,
but the oxide of lead and oxide of bismuth remain yellow.

f. CARBONIZATION TAKES PLACE : organic substances. **9**
If the residue effervesces when drenched with acids, whilst
the original substance does not, this indicates the presence
of ORGANIC ACIDS, combined with alkalies or alkaline
earths.   Odor of cyanogen indicates the presence of a
CYANIDE.

Many substances swell up considerably upon the appli-
cation of heat ; such are, for instance, borax, sulphate of
alumina, &c.; others crepitate. e. g. chloride of sodium,
and chloride of potassium, &c. ; these phenomena, how-
ever, are of a less conclusive nature than the preceding.

3. A small portion of the substance is put on a charcoal **10**
support, and exposed to the reducing flame of the blow-pipe.
Since most of the phenomena just now described, § 107, 2 (3),
are also produced by this process, I will enumerate here only
those which result more particularly and exclusively from its
application.

a. THE SUBSTANCE VOLATILIZES PARTLY OR COM- **11**
PLETELY.   This indicates, besides the substances men-
tioned in § 107. 2. *d.* (7), also OXIDE OF ANTIMONY, and
several other oxides. (Compare § 107. 3. *d.* *β.* (16). The
oxide of antimony fuses previously to volatilizing in the
form of a white vapor.   The presence of ARSENIOUS or
ARSENIC ACID is indicated by the characteristic odor of
garlic, which is rendered more strongly perceptible by
adding carbonate of soda to the sample before exposing it
to the blow-pipe flame.

b. THE BODY FUSES, AND IS IMBIBED BY THE CHAR- **12**
COAL ; this indicates the presence of ALKALIES.   In this
case, a portion of the finely powdered substance is placed
upon the moistened loop of a platinum wire, and the
point of the inner flame is directed upon it. If the oxidiz-
ing flame assumes a violet tint, this indicates the pre-

sence of POTASSA alone; if a yellow tint, the presence of SODA, with which potassa may however, be mixed, even in considerable proportion, since the flame appears invariably yellow when both these alkalies are present.

c. THE SUBSTANCE LEAVES AN INFUSIBLE WHITE **13** RESIDUE ON THE CHARCOAL, EITHER AT ONCE, OR AFTER PREVIOUS MELTING IN THE WATER OF CRYSTALLIZATION; this indicates more particularly the presence of baryta, strontia, lime, magnesia, alumina, oxide of zinc, and silicic acid. Among these substances, STRONTIA, LIME, MAGNESIA, and oxide of ZINC, are distinguished by strong luminosity in the blow-pipe flame. The white residue is moistened with a drop of solution of protonitrate of cobalt, and then again strongly ignited. If the mass assumes a fine blue tint, this indicates the presence of ALUMINA; if a reddish tint, of MAGNESIA; if a green color, of ZINC. When SILICIC ACID is present, the mass also assumes a faint bluish tint, which should not be confounded with that proceeding from the presence of alumina. Silicic acid is characterized moreover by the formation of a clear bead, attended with effervescence, upon exposing this acid, with carbonate of soda, to a strong blow-pipe flame, § 100. b. 4, as well as by its behaviour with phosphate of soda, § 100. b. 5.

d. THE SUBSTANCE LEAVES AN INFUSIBLE RESIDUE **14** OF A DIFFERENT COLOR, OR A REDUCTION TO THE METALLIC STATE TAKES PLACE, WITH OR WITHOUT INCRUSTATION OF THE CHARCOAL SUPPORT. A portion of the powder is mixed with carbonate of soda, and heated on charcoal in the reducing flame.

α. The continued application of a strong flame pro- **15** duces a metallic bead, without incrustation of the charcoal; this indicates the presence of GOLD, SILVER, TIN, or COPPER. The compounds of platinum, iron, cobalt, and nickel, are likewise reduced, but yield no metallic beads.

β. The charcoal support is coated over with an in- **16** crustation, either with or without simultaneous forma-

tion of a metallic grain; this indicates the presence of
BISMUTH, LEAD, CADMIUM, ANTIMONY, or ZINC.

aa. If the incrustation is white, ANTIMONY OR **17**
ZINC may be supposed to be present. That pro-
duced by zinc appears yellow as long as it remains
hot. The pure metallic bead of antimony continues
to evolve white vapors, even for a long time after all
application of heat has been withdrawn, and upon
cooling generally becomes surrounded with crystals
of oxide of antimony. It is brittle under the stroke
of the hammer.

bb. The incrustation is more or less yellow or **18**
brown; this indicates the presence of BISMUTH,
LEAD, or CADMIUM. The yellow incrustation of oxide
of cadmium inclines slightly to orange; the brown-
ish yellow incrustation of oxide of lead and oxide of
bismuth change to a light yellow upon cooling.
Upon reduction, cadmium volatilizes immediately.
The globules of lead are very malleable, whilst those
of bismuth are brittle under the stroke of the
hammer.

4. A small portion is fused with a bead of microcosmic salt, **19**
and exposed to the outer flame of the blow-pipe.

a. THE SUBSTANCE DISSOLVES READILY AND IN CON-
SIDERABLE QUANTITY, FORMING, WHILST HOT, A CLEAR
BEAD.

a. The fused bead is colored, blue by candle light, **20**
inclining to violet, COBALT: green, very bright on cool-
ing, unaltered in the reducing flame, CHROMIUM:
green, on cooling blue, and becoming red in the re-
ducing flame, COPPER: reddish-brown, on cooling
clear yellow, or colorless, in the reducing flame a
bottle-green, IRON: dark yellow, inclining to red, on
cooling becoming clearer or colorless, unaltered in the
reducing flame, especially on the addition of a little
tin, almost colorless, and on cooling of a blackish-grey,
BISMUTH: clear yellow inclining to opal; when cold
rather dull, in the reducing flame greyish-white, SILVER:

amethyst red, especially on cooling; unaltered by fusing in the outer flame; in the reducing flame color-less and not quite clear, MANGANESE.

β. *The fused bead is colorless;* remains clear on 21 cooling, ANTIMONY, ALUMINA, ZINC, CADMIUM, LEAD, LIME, MAGNESIA : a great excess of the last five ren-ders the bead enamel white; when saturated with oxide of lead it becomes yellow. The addition of a very small portion renders the lead enamel white on cooling, BARYTA or STRONTIA.

b. THE SUBSTANCE DISSOLVES BUT SLOWLY AND IN 22 SMALL QUANTITY.

a. The bead is colorless both whilst hot and on cool-ing; the addition of a little peroxide of iron causes the characteristic color of iron to be developed, SILICA.

β. The bead is colorless, remaining so after the ad-dition of some peroxide of iron, TIN.

c. THE SUBSTANCE DOES NOT DISSOLVE BUT SWIMS 23 (AS A METAL) IN THE PEARL, GOLD, PLATINA.

The student must be prepared, of course, to meet with the manifestation of mixed phenomena, arising from the inter-mixture, or combination of many different substances, and he must therefore be guarded in his conclusions, since it is impos-sible to give defined and characterized cases, which will at the same time offer the advantage of general applicability.

II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. A small portion of the substance is heated with water, 24 acidulated with acetic acid.

a. HYDROGEN GAS IS EVOLVED; this indicates the presence of a light metal and possibly of manganese. The presence of alkalies and of alkaline earths must be had regard to in the actual examination.

b. No HYDROGEN IS EVOLVED; this indicates the absence of light metals. Alkalies and alkaline earths may be alto-gether disregarded in the course of the special investigation.

2. A portion of the substance is heated on charcoal, in the 25

reducing flame of the blow-pipe, and the ensuing phenomena are carefully watched; for instance, whether the substance fuses, if an incrustation is formed, or an odor emitted, &c.

a. THE SUBSTANCE REMAINS UNALTERED; this is pretty conclusive of the absence of antimony, zinc, lead, bismuth, cadmium, tin, mercury, and arsenic; the absence of gold, silver, and copper, is also probable; it indicates the presence of PLATINUM, IRON, MANGANESE, NICKEL, or COBALT.

b. THE SUBSTANCE FUSES WITHOUT SIMULTANEOUS INCRUSTATION, AND WITHOUT ODOR; absence of antimony, zinc, lead, bismuth, cadmium, and arsenic; presence of GOLD, SILVER, COPPER, or TIN.

c. THE SUBSTANCE FUSES, AND AN INCRUSTATION IS FORMED, BUT NO ODOR EMITTED; absence of arsenic, and presence of ANTIMONY, ZINC, BISMUTH, LEAD, or CADMIUM. (Compare § 107, I. 3, *d.* β). (16).

d. THE SUBSTANCE EMITS THE ODOR OF GARLIC; ARSENIC is present. For the other phenomena which may manifest themselves, I refer to *a. b.* or *c.* (25).

3. A portion of the substance is heated before the blow-pipe 26 in a glass tube, sealed at one end.

a. NO SUBLIMATE IS FORMED IN THE COLDER PART OF THE TUBE; absence of mercury.

b. A SUBLIMATE IS FORMED; presence of MERCURY, CADMIUM, or ARSENIC. The sublimate of mercury, which consists of small globules, cannot possibly be confounded with that of cadmium or arsenic.

§ 108.

B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. A small portion of the fluid is evaporated in a platinum 27 spoon, or in a small porcelain crucible, to ascertain in the first place whether the fluid contains any matter in solution; the nature of the residue is then examined according to the directions given at § 107.

2. The fluid is tested with litmus paper (blue and reddened). 28

a. THE FLUID REDDENS BLUE LITMUS PAPER. This

reaction may be caused by a free acid, an acid salt, or by a soluble metallic salt. In order to distinguish between these cases, a small quantity of the fluid is poured into a watch-glass, and a little rod, the extreme point of which has previously been dipped into dilute solution of carbonate of potassa, placed in it; if the fluid remains clear, or if the precipitate which may form at first, redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes turbid and remains so, this generally denotes the presence of a soluble metallic salt. As a matter of course, a solution which contains a free acid or an acid salt can no longer be considered simply aqueous, and the subsequent examination must accordingly be conducted with due regard to the possible presence of substances insoluble in water but soluble in acids.

b. REDDENED LITMUS PAPER TURNS BLUE; this indi- **29** cates the presence of free alkalies or alkaline carbonates, free alkaline earths, alkaline sulphurets, and of a number of other salts. Substances dissolved in fluids containing a free alkali, may belong to the class of bodies either soluble or insoluble. The way in which this point is to be settled, and further information on the subject of alkaline solutions in general, will be found at § 117, I. 2, **(104).**

3. The fluid is examined by smelling and tasting, or, should **30** this fail to yield satisfactory results, by distillation, to prove whether the simple solvent present is water, alcohol, ether, &c. If it is found not to be water, the solution is evaporated to dryness, and the residue treated according to § 107.

4. If the solution happen to be aqueous, and manifests an **31** acid reaction, a portion of it is highly diluted with water. Should this addition of water to the fluid impart a milky and turbid appearance to the latter, the presence of ANTIMONY, BISMUTH, OR TIN, may be inferred. If the precipitate disappears upon the addition of tartaric acid, we may conclude that antimony is present, whilst its persistence with tartaric, and re-solution by acetic acid, indicates the presence of bismuth.

The original fluid is then treated either as directed at § 110, or at § 117, according to whether the operator has reason to suppose it to be the solution of a simple, compound, or mixed substance.

II. SOLUTION OF BODIES OR CLASSIFICATION OF SUBSTANCES ACCORDING TO THEIR DEPORTMENT WITH CERTAIN SOL-VENTS.

§ 109.

Water and hydrochloric acid, or in certain cases nitric acid, 32 are the solvents used to classify simple, or compound sub-stances, and to isolate the component parts of mixtures. We divide the various substances into three classes, according to their respective behaviour with these solvents.

First class.—SUBSTANCES SOLUBLE IN WATER.

Second class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC, OR NITRIC ACID.

Third class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE, IN WATER AND HYDROCHLORIC OR NITRIC ACID.

The solution of alloys being more appropriately effected in a different manner from that pursued with other bodies, I shall give a special method for these substances. (§ 109, B.) (**43**).

The process of solution or separation is conducted in the following manner.

A. THE SUBSTANCE UNDER EXAMINATION IS NEITHER A METAL NOR AN ALLOY.

1. About fifteen or twenty grains of the finely powdered **33** substance under examination, are covered in a test-tube with from ten to twelve times their amount of distilled water, and the mixture is heated to boiling over a spirit-lamp.

a. THE SUBSTANCE DISSOLVES COMPLETELY. In this case it belongs to the first class; regard must be had to what has been stated in § 108, 2 (**28**), concerning re-actions. The solution is treated either as directed at

§ 110, or at § 117, as either one or several acids and bases are supposed to be present.

b. AN INSOLUBLE RESIDUE, EVEN AFTER PROTRACTED **34** BOILING, is allowed to subside, and the fluid filtered off if possible in such a manner as to leave the residues in the test-tube ; a few drops of the clear filtrate are then evaporated on a clean platinum plate ; if nothing remains, the substance is completely insoluble in water, and is then further treated as directed at § 109, 2, **(35)**. But if a residue occurs, the substance is at least partly soluble. The first residue is in that case once more boiled with water, the fluid is filtered off, and the filtrate added to the original solution, which is then treated, according to circumstances, as directed at § 110, or at § 117. The residue is washed with water, and treated in conformity with the directions of § 109, 2, **(35)**.

2. The residue of *b.* **(34)**, is drenched with dilute hydro- **35** chloric acid. If it prove insoluble, the mixture is to be heated to the boiling point, and should even this fail to effect a perfect solution, the fluid is to be decanted, and the residue boiled with concentrated hydrochloric acid.

The phenomena which may manifest themselves in this operation, and which ought to be carefully observed are, *a.* Effervescence, which indicates the presence of carbonic acid, or sulphuretted hydrogen, (vide § 111. 2. **(68)** ; *β.* Evolution of chlorine, with indicates the presence of hyperoxides, chromates, &c. ; *γ.* Emission of the odor of hydrocyanic acid, which indicates the presence of insoluble cyanides. To the decomposition of the latter, a special paragraph will be devoted. (Vide § 131.)

a. THE RESIDUE IS COMPLETELY DISSOLVED BY THE **36** HYDROCHLORIC ACID, with the separation of sulphur (known by its color and light specific weight) or of hydrated silicic acid ; the solution is treated, according to circumstances, either as directed at § 113, or § 118. The substance belongs to the second class. When the presence of silica is known or suspected (§ 107. I. 4. *b.*) **(22)**, it is

better to evaporate to dryness, treat the residue with hydrochloric acid and gently warm, then after adding some water, filter from the now insoluble silica, which may be further tested according to § 100. *b.* The clear liquid to be treated as above directed.

b. THERE IS STILL A RESIDUE. In this case the test- **37** tube containing the specimen which has been boiled with the hydrochloric acid, is put aside pro tempore, and another portion of the substance under examination is boiled in nitric acid, with subsequent addition of water.

a. The specimen is completely dissolved, or sulphur **38** *and the gelatinous hydrate of silicic acid may remain undissolved;* the body in these cases belongs to the second class; this solution is then further tested for bases, (should silica occur or be suspected, the liquid must first be treated as directed in the present, § 2. *a.*) (36), according to circumstances, either as directed § 113, or in conformity to the directions of § 117. III **(109)**.

β. After boiling with nitric acid there is still a residue. **39**
    aa. THE OPERATOR HAS REASON TO SUPPOSE THAT THE SUBSTANCE UNDER EXAMINATION CONTAINS ONLY *one* BASE AND *one* ACID. The substance is drenched with aqua regia, and heat applied.

    aa. The substance dissolves. The solution is treated according to § 113.

    ββ. The substance does not dissolve. In that case the operator has to proceed according to the directions given at § 116.

    bb. THE OPERATOR HAS REASON TO SUPPOSE **40** THAT THE SUBSTANCE UNDER EXAMINATION IS A COMPLEX COMPOUND OR MIXTURE. In this case the reserved hydrochloric solution (§ 109. A. 2. *b.* (**37**) is tested for the bases. It is for this purpose heated to boiling with the insoluble residue—(which latter is afterwards to be treated as directed at § 109. 3. (**42**)—and filtered hot into a tube containing some water; the residue is then again boiled with water,

the fluid filtered off whilst hot, and added to the hy-
drochloric acid solution.   If the presence of silica is
suspected, evaporate the solution to dryness, and
warm with a little hydrochloric acid, afterwards add-
ing water.

 aa. The filtrate becomes turbid and milky; **41**
this indicates ANTIMONY and BISMUTH; or it depo-
sits fine crystals: this indicates the presence of
LEAD. The filtrate is heated (if necessary, with
the addition of some hydrochloric acid) until it
clears again; the further process is conducted ac-
cording to the directions of § 118.

 ββ. The filtrate remains clear. A few drops
of it are evaporated to ascertain beyond doubt
whether the hydrochloric acid has really dissolved
anything.   If there be a residue, the filtrate is
treated according to § 118.

  3. Should the boiling concentrated hydrochloric acid have **42**
left a residue, this is washed with water, and treated as directed
§ 130.

B. THE SUBSTANCE UNDER EXAMINATION IS A METAL OR **43**
AN ALLOY.

   The metals are best divided according to their behaviour
with nitric acid.

   I. METALS WHICH ARE NOT AFFECTED BY NITRIC ACID :
gold, platinum.
   II. METALS WHICH ARE OXIDIZED BY NITRIC ACID, BUT
OF WHICH THE OXIDES DO NOT DISSOLVE IN EXCESS OF THE
ACID : antimony, tin.
   III. METALS WHICH ARE OXIDIZED BY NITRIC ACID, AND
OF WHICH THE OXIDES DISSOLVE IN AN EXCESS OF THE
ACID, FORMING NITRATES : all other metals.
   Nitric acid of 1.25 sp. gr. is poured over the metal or alloy
under examination, and heat applied.

1. COMPLETE SOLUTION TAKES PLACE EITHER AT ONCE OR **44**
UPON THE ADDITION OF WATER: this proves the absence of
(platinum) gold, antimony, and tin : a small portion of the
solution is diluted with a copious amount of water.

> *a. The solution remains clear*; some hydrochloric
> acid is added. If this produces a white precipitate, inso-
> luble upon heating the fluid, but which, after previous
> washing, is dissolved by ammonia, SILVER is present. The
> original solution is treated, as directed at § 118.
>
> *b. The solution becomes turbid and milky;* this indi-
> cates the presence of BISMUTH. The solution is filtered,
> and the filtrate tested for silver, as at *a.* The original
> solution is finally treated according to § 118.

2. THERE IS A RESIDUE.   **45**

> *a. The residue is metallic.* The solution is filtered,
> and the filtrate treated as directed at § 109. B. 1. (**44**),
> after having examined, in the first place, whether any-
> thing has been dissolved. The residue is thoroughly
> washed, and then dissolved in aqua regia; the solution
> is divided into two portions ; and chloride of potassium
> added to the one part; if a yellow precipitate is formed,
> this indicates the presence of PLATINUM. Protosulphate
> of iron is added to the other portion : if a black precipi-
> tate is formed, this indicates the presence of GOLD.
>
> *b. There is a white pulverulent residue ;* this indicates **46**
> the presence of ANTIMONY and TIN. The solution is
> filtered, and the filtrate treated as directed at § 109. B. 1.
> (**44**), after having examined, in the first place, whether
> anything has been dissolved. The residue is thoroughly
> washed and heated with a hot saturated solution of bitar-
> trate of potassa, or with a solution of tartaric acid.
>
> > *a.* Complete solution takes place : this indicates the **47**
> > presence of oxide of ANTIMONY alone ; the solution is
> > tested with sulphuretted hydrogen.
> >
> > *β.* A white precipitate remains, even after boiling
> > with a fresh portion of solution of bitartrate of potassa
> > or tartaric acid ; this indicates the probable presence

P

of TIN. The solution is filtered, and the filtrate treated,
in the first place, with some hydrochloric acid, and
afterwards with solution of sulphuretted hydrogen. If
an orange-red precipitate is formed, OXIDE OF ANTI-
MONY is present. It is invariably necessary that the
operator should satisfy himself whether the residue
consists really of peroxide of tin; this may be clearly
ascertained by mixing it with cyanide of potassium, and
carbonate of soda, and reducing it before the blow-pipe
(Compare § 95. c. 7).

III. ACTUAL EXAMINATION.

*Compounds supposed to consist simply of one base and one acid ;
or of one metal, and one metalloid.*

A. SUBSTANCES SOLUBLE IN WATER.

Detection of the base. *

§ 110.

1. Some hydrochloric acid is added to a portion of the aque- **48**
ous solution.

    a. No PRECIPITATE IS FORMED ; this is a positive proof
of the absence of silver and protoxide of mercury, and is
likewise an indication of the probable absence of lead.
The acidified solution is treated according to the direc-
tions of § 110. 2. (**50**).

    b. A PRECIPITATE IS FORMED. Divide the fluid, in **49**
which the precipitate is suspended into two portions, and
add ammonia in excess to the one.

    a. *The precipitate redissolves, and the fluid becomes
clear ;* this shows the precipitate to have consisted of
chloride of silver, and is consequently indicative of the
presence of SILVER. To arrive at a positive conviction
on this point, the original solution must be tested with

    * We include here arsenious and arsenic acids.

chromate of potassa, and with sulphuretted hydrogen.
(Vide § 91. *a.* 3, and 97. *b.* 6).

β. *The precipitate becomes black ;* this shows the
precipitate to have consisted of protochloride of mer-
cury, which has now been converted by the ammonia
into protoxide of mercury ; it is consequently indica-
tive of the presence of PROTOXIDE OF MERCURY. To
set all doubt on this point at rest, the original solution
is tested with protochloride of tin, and with metallic
copper. (Vide § 91. *b.*)

γ. *The precipitate remains unaltered;* it consists in
this case of chloride of lead, which is neither decom-
posed nor dissolved by ammonia; this reaction is ac-
cordingly indicative of the presence of LEAD. Whether
the precipitate consists really of chloride of lead or not
is conclusively ascertained : 1st, by diluting the se-
cond portion of the fluid in which the precipitate pro-
duced by hydrochloric acid is suspended, with a large
amount of water and applying heat ; the precipitate
must dissolve if it consists really of chloride of lead ;
and 2nd, by adding dilute sulphuric acid to the ori-
ginal solution, (§ 91. *c.*)

2. The acidified fluid of 1. *a.* is mixed with solution of sul- **50**
phuretted hydrogen until it smells distinctly of that gas, even
after continued agitation ; heat is then applied to the mixture.

a. THE FLUID REMAINS CLEAR.   Pass over to 3. **(56)**,
since this is a proof that lead, bismuth, copper, cadmium,
peroxide of mercury, gold, platinum, tin, antimony, ar-
senic, and peroxide of iron, are not present.

b. A PRECIPITATE IS FORMED.

a. THIS PRECIPITATE IS WHITE; it consists in this **51**
case of separated sulphur, and is indicative of the pre-
sence of PEROXIDE OF IRON (§ 89. *f.*)   However, as
the separation of sulphur may also be caused by other
substances, it is indispensable that the operator should
satisfy himself whether the substance present is really
peroxide of iron or not.   For this purpose the original

P 2

solution is to be tested with ammonia, and with ferro-
cyanide of potassium.

β. THE PRECIPITATE IS YELLOW; in this case it **52**
may consist either of sulphuret of cadmium, sulphuret
of arsenic, or bisulphuret of tin; it indicates accord-
ingly the presence of either cadmium, arsenic, or
peroxide of tin. To distinguish between them, ammonia
in excess is added to a portion of the fluid, wherein
the precipitate is suspended.

aa. The precipitate does not disappear; it con-
sists of CADMIUM; for sulphuret of cadmium is in-
soluble in ammonia. The blow-pipe is resorted to
as a confirmatory test. (§ 92. *d.*)

bb. The precipitate disappears. It consists either
of peroxide of tin or of arsenic. Ammonia is added
to a portion of the original solution.

aa. A white precipitate is formed. PEROXIDE
OF TIN is the substance present. Positive convic-
tion is obtained by reducing the precipitate before
the blow-pipe, with cyanide of potassium and car-
bonate of soda. (§ 95. *c.*)

ββ. No precipitate is formed. This indicates
the presence of ARSENIC. Positive conviction may
be arrived at by the production of an arsenical
mirror, which is effected by reducing the original
substance, or the precipitated sulphuret of arsenic,
either with cyanide of potassium and carbonate of
soda, or in some other way; and by exposing the
original substance with carbonate of soda to the
inner flame of the blow-pipe. (§ 95. *d.*)

γ. THE PRECIPITATE IS ORANGE-COLORED; in this **53**
case it consists of sulphuret of antimony, and indi-
cates the presence of OXIDE OF ANTIMONY. Reduction
before the blow-pipe is resorted to for confirmation.
(§ 95. *a.*)

δ. THE PRECIPITATE IS BROWN. It consists of pro- **54**
tosulphuret of tin, and indicates the presence of PRO-

TOXIDE OF TIN. To remove all doubt on this point, one portion of the original solution is tested with solution of perchloride of mercury, and another with solution of perchloride of gold. (§ 95. *b*.)

ε. THE PRECIPITATE IS BLACK. It may in this case **55** consist either of sulphuret of lead, sulphuret of copper, sulphuret of bismuth, sulphuret of gold, sulphuret of platinum, or bisulphuret of mercury. To distinguish between these different sulphurets, the following experiments are to be had recourse to.

aa. Dilute sulphuric acid is added to a portion of the original solution : a white precipitate is formed; this indicates LEAD. Chromate of potassa is employed as a conclusive test. (§ 91. *c*.)

bb. Ammonia in excess is added to a portion of the original solution. A blue precipitate is formed which redissolves in an excess of the precipitant, imparting an azure colour to the fluid; this indicates COPPER. Ferrocyanide of potassium is resorted to as a conclusive test. (§ 92. *b*.)

cc. Potassa is added to a portion of the original solution; a yellow precipitate is formed; this indicates PEROXIDE OF MERCURY. Protochloride of tin and metallic copper are applied as conclusive tests. (§ 92. *a*.) The presence of peroxide of mercury is usually sufficiently indicated by the several changes of color through which the precipitate produced by the sulphuretted hydrogen water in the fluid under examination is observed to pass; this precipitate is white at first, but passes, upon the addition of an excess of the precipitant, from yellow to orange, and becomes finally black. (§ 92. *a*. 3).

dd. A portion of the original solution is evaporated nearly to dryness, in a porcelain crucible, and the residue washed into a test-tube, half filled with water. If the solution becomes milky, a basic salt of bismuth is present; this reaction, consequently, indi-

cates BISMUTH. The blow-pipe is resorted to as a conclusive test. (§ 92. *c*.)

ee. Solution of protosulphate of iron is added to a portion of the original solution. A fine black precipitate is indicative of the presence of GOLD. To remove all doubt as to the nature of this precipitate, the blow-pipe is resorted to ; or the original solution is tested with protochloride of tin. (§ 94. *a*.)

ff. Chloride of potassium is added to·a portion of the original solution ; the formation of a yellow crystalline precipitate is indicative of the presence of PLATINUM. To remove all doubt on this point, the precipitate is ignited. (§ 94. *b*.)

3. A portion of the original solution is mixed with chloride **56** of ammonium, and ammonia added to alkaline reaction ; it is then treated with hydrosulphuret of ammonia, no matter whether a precipitate formed upon the addition of ammonia, or not.

a. No PRECIPITATE IS FORMED ; pass over to § 110. 4. **(62)** ; for iron, cobalt, nickel, manganese, zinc, chromium, and alumina are not present.

b. A PRECIPITATE IS FORMED.

a. *The precipitate is black* ; protoxide of iron, **57** nickel, or cobalt. A portion of the original solution is mixed with caustic potassa.

aa. A dirty greenish-white precipitate is formed, which soon changes to a reddish-brown, when exposed to the air : PROTOXIDE OF IRON. Ferricyanide of potassium is resorted to as a conclusive test. (§ 89. *e*.)

bb. A precipitate of a light greenish tint is produced, which does not change its color : NICKEL. Ammonia, with subsequent addition of potassa, is resorted to as a conclusive test. (§ 89. *c*.)

cc. A sky-blue precipitate is formed, which, upon boiling, becomes reddish : COBALT. The blow-pipe is resorted to as a conclusive test. (§ 89. *d*.)

β. The precipitate is not black.   **58**

aa. If the precipitate is distinctly flesh-colored, it consists of sulphuret of manganese, and is consequently indicative of the presence of PROTOXIDE OF MANGANESE. The addition of potassa to the original solution, or the blow-pipe, are resorted to as conclusive tests. (§ 89. *b.*)

bb. If the precipitate is bluish-green, it consists of hydrated OXIDE OF CHROMIUM. The addition of potassa to the original solution, and the blow-pipe, are resorted to as conclusive tests. (§ 88, *b.*)

cc. If the precipitate is white, it may consist either **59** of hydrate of alumina, or of sulphuret of zinc, and thus indicate the presence of either alumina or oxide of zinc. To distinguish between these two oxides, solution of potassa is gradually dropped into a portion of the original fluid, till the precipitate which forms is redissolved ; and

aa. Sulphuretted hydrogen water is then added to a portion of this solution; the formation of a white precipitate indicates the presence of ZINC. As a conclusive test, the reaction with solution of protonitrate of cobalt before the blow-pipe is selected. (§ 89. *a.*)

ββ. Chloride of ammonium is added to another portion of the potassa solution. The formation of a white precipitate indicates the presence of ALUMINA. The test with solution of protonitrate of cobalt before the blow-pipe is conclusive. (88. *a.*)

Note to § 110. 3. *b.* *β.* (58).   **60**

As very slight contaminations may impair the distinctness of the tints exhibited by the precipitates considered at § 110. 3. *b.* *β.* (58), it is advisable, in all cases where the slightest

impurity is suspected, to adopt the following method for the detection of manganese, chromium, zinc, and alumina.

Potassa in excess is added to a portion of the original solution

> *aa.* A whitish precipitate is formed, which does not redissolve in an excess of the precipitant, and changes its color speedily to a blackish-brown when exposed to the air : MANGANESE. The blow-pipe is resorted to as a conclusive test. (§ 89. *b.*)

> *bb.* A precipitate is formed which redissolves in an **61** excess of the precipitant : OXIDE OF CHROMIUM, ALUMINA, ZINC.

> > *aa.* Sulphuretted hydrogen water is added to a portion of the potassa solution. The formation of a white precipitate indicates the presence of ZINC.

> > *ββ.* If the original solution, or the potassa solution is green, and the precipitate, produced by potassa and redissolved by excess of the precipitant, is of a bluish color, OXIDE OF CHROMIUM is present. To remove all doubt on this point, the potassa solution is heated to ebullition, or the blow-pipe resorted to. (§ 88. *b.*)

> > *γγ.* Chloride of ammonium is added to the potassa solution. The formation of a white precipitate indicates the presence of ALUMINA. The test with solution of cobalt before the blow-pipe is conclusive. (§ 88. *a.*)

4. Chloride of ammonium and carbonate of ammonia, mixed **62** with a small quantity of caustic ammonia, are added to a portion of the original solution, and gentle heat applied.

> *a.* No PRECIPITATE IS FORMED : absence of baryta, strontia, and lime. Pass over to § 110, 5, (**64**).

> *b.* A PRECIPITATE IS FORMED : presence of baryta, **63** strontia, or lime.

Solution of sulphate of lime is added to a portion of the original solution, and heat applied.

> *a. The solution does not become turbid, even after*

the lapse of from five to ten minutes : LIME. The test with oxalic acid is selected as a confirmatory proof. (§ 87. *c.*)

β. *The solution becomes turbid after the lapse of some time :* STRONTIA. The alcohol flame is resorted to as a conclusive test. (§ 87. *b.*)

γ. *A precipitate is immediately formed :* BARYTA. To remove all doubt on this point, test with hydrofluosilicic acid. (§ 87. *a.*)

5. Phosphate of soda is added to the solution of 4, *a.* (62), **64** in which carbonate of ammonia has failed to produce a precipitate, after previous addition of chloride of ammonium.

a. No PRECIPITATE IS FORMED, even after agitating the solution : absence of magnesia. Pass over to § 110. 6. **(65)**.

b. A CRYSTALLINE PRECIPITATE IS FORMED : MAGNESIA.

6. A drop of the original solution is evaporated on a plati- **65** num plate and the residue ignited.

a. THERE IS NO FIXED RESIDUE. Hydrate of lime is added to the original solution. The odor and reaction of the escaping gas, and the fumes which it forms with acetic acid, will prove the presence of AMMONIA. (§ 86. *c.*)

b. THERE IS A FIXED RESIDUE. Potassa or soda. A **66** portion of the original solution is mixed with tartaric acid and well shaken. (Should the original solution be highly diluted, it will be necessary, in the first place, to concentrate it by evaporation).

α. *No precipitate is formed, even after the lapse of ten or fifteen minutes :* SODA. The blow-pipe flame and alcohol flame are selected as conclusive tests. (§ 86. *b.*)

β. *A crystalline granular precipitate is formed :* POTASSA. Bichloride of platinum, the blow-pipe flame, and alcohol flame, are selected as conclusive tests. § 86. *a.*)

*Compounds which are supposed to contain but one acid
and one base, &c.*

A. SUBSTANCES SOLUBLE IN WATER.   DETECTION OF THE ACID.

I. *Detection of inorganic acids.*

§ 111.

The analyst should in the first place reflect *which* of the
inorganic acids form soluble compounds with the detected
base, and to bear this carefully in mind in his subsequent
operations.

1. I have already spoken of ARSENIOUS ACID and ARSENIC **67**
ACID while treating of the detection of the bases, These two
acids are distinguished from each other by their respective be-
haviour with nitrate of silver, or with potassa and sulphate of
copper. (§ 95, *d.* and *e.*)

2. While pursuing the systematic course for the determina- **68**
tion of the bases, the operator is led to the detection of CAR-
BONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID.   The
two former betray their presence by effervescing upon the
addition of hydrochloric acid; they may be distinguished from
one another by their odor.   Should additional proof be re-
quired, the presence of carbonic acid may be ascertained
beyond doubt by the reaction with lime water (vide § 100. *a.*),
and that of sulphuretted hydrogen by the reaction with solu-
tion of lead. (§ 101. *e.*)   Chromic acid may invariably be
detected by the yellow or red tint of the solution, and likewise
by the transition of this red or yellow color to green, attended
with separation of sulphur, upon the addition of sulphuretted
hydrogen water.   To remove all doubt on this point, the reac-
tions with solution of acetate of lead and solution of nitrate of
silver may be finally resorted to. (§ 97. *b.*)

3. Chloride of barium is added to a portion of the solution, **69**
which, should its reaction be acid, is first to be neutralized, or
rendered feebly alkaline, by addition of ammonia.

    a. THE FLUID REMAINS CLEAR.   Pass over to § 111.

4. (**71**). The absence of sulphuric acid, phosphoric acid, and silicic acid is certain, that of oxalic acid and boracic acid probable. The baryta compounds of the two latter acids are kept in solution by ammoniacal salts, whilst borate of baryta does not separate from *dilute* solutions, even though no ammoniacal salts be present.

   b. A PRECIPITATE IS FORMED. Dilute hydrochloric **70** acid is added in excess.

      a. The precipitate dissolves. Absence of sulphuric acid. Pass over to 4. (**71**).

      β. The precipitate remains undissolved, even though a considerable quantity of water be added : SULPHURIC ACID.

4. Solution of sulphate of lime is added. To a portion of **71** the original solution, (which, should it have an acid reaction, is first to be rendered neutral or feebly alkaline, by ammonia), and if no ammoniacal salt be present, some sal ammoniac must be added.

   a. No PRECIPITATE IS FORMED : absence of oxalic acid and phosphoric acid. Pass over to § 111. 5. (**73**).

   b. A PRECIPITATE IS FORMED. Acetic acid is added in **72** excess.

      a. The precipitate is redissolved : PHOSPHORIC ACID. The reactions with sulphate of magnesia and ammonia, with solution of nitrate of silver, and the blow-pipe, are used as conclusive tests. (§ 99. *a.*)

      β. The precipitate remains undissolved, but is readily soluble in hydrochloric acid : OXALIC ACID. The reaction with concentrated sulphuric acid is selected as a conclusive test. (§ 99, *c.*)

5. A fresh portion of the original solution is acidified with **73** nitric acid, and solution of nitrate of silver added.

   a. THE FLUID REMAINS CLEAR. This is a certain indication of the absence of chlorine and iodine; that of cyanogen is also probable. (Of the soluble metallic cyanides, percyanide of mercury is not precipitated by nitrate of silver; and from the nature of the detected

base, the operator may judge whether the presence of
cyanogen is possible or probable; for the manner in
which it is detected in the percyanide of mercury I refer
to § 101, *d*.   Pass over to § 111. 6. (**75**).

b. A PRECIPITATE IS FORMED.   Ammonia is added in **74**
excess.

 a. The precipitate does not dissolve : IODINE.   As
a conclusive test we select the reaction with starch.
(§ 101. *c*.)

 β. The precipitate redissolves.   If this occurs
readily, there is reason to suppose that CHLORINE is
present; if it dissolves with difficulty and only upon
the addition of a large portion of ammonia, it is pro-
bably a CYANIDE.   The presence of chlorine may be
ascertained beyond doubt, by testing the original solu-
tion with protonitrate of mercury, and by the deport-
ment of the silver precipitate at a high temperature.
(§ 101. *a*.)   The presence of cyanogen may be ascer-
tained positively by adding potassa, solution of ferroso-
ferric oxide, and hydrochloric acid to the original
solution. (§ 101. *d*.)

6. A portion of the solid substance—(or, should the body .**75**
to be examined exist in the fluid state, *the residue after evapo-
ration*)—is drenched with some sulphuric acid; alcohol is
then added and kindled.   Should the flame appear green
upon stirring, this is a proof of the presence of BORACIC ACID.

7. With regard to the presence of nitric acid, this is usually **76**
discovered in the course of the preliminary examination,
(vide § 107. I. 2. *c*.) (**6**).   To ascertain the presence of this
acid beyond doubt, the reaction with protosulphate of iron and
sulphuric acid, or that with solution of indigo, are resorted to.
(§ 102. *a*.)

8. I refer to § 126 for the detection of chloric acid, hydro- **77**
fluoric acid, silicic acid, and bromine.

Compounds which are supposed to contain only one acid and one   ⌐2—
base, &c.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF
THE ACID.

II. *Detection of organic acids.*

§ 112.

1. To a portion of the aqueous solution of the compound **78** under examination, ammonia is added to feeble alkaline reaction, and afterwards chloride of calcium. Should the solution be neutral, the addition of the chloride of calcium is to be preceded by that of some chloride of ammonium.

a. NO PRECIPITATE IS FORMED, NEITHER AFTER AGI-
TATING THE SOLUTION, NOR AFTER THE LAPSE OF A FEW
MINUTES: absence of oxalic acid and tartaric acid. Pass
over to § 112. 2. (**80**).

b. A PRECIPITATE IS FORMED. Lime-water is added **79**
in excess to a portion of the original solution, and the
precipitate formed is acted upon with solution of chloride
of ammonium.

a. *The precipitate redissolves*: TARTARIC ACID. The
reaction with acetate of potassa may be resorted to as a
confirmatory test; but a still more positive proof will
-be afforded by the deportment which the precipitate
produced by the chloride of calcium, exhibits with
caustic potassa. (§ 103. *b.*)

β. *The precipitate does not redissolve :* OXALIC
ACID. The reaction of concentrated sulphuric acid is
selected as a conclusive test. (§ 99. *c*).

2. The fluid of 1. *a.* (**78**) is heated to boiling, maintained **80**
so for some time, and whilst in this state more ammonia is
added.

a. IT REMAINS PERFECTLY TRANSPARENT: absence of
citric acid. Pass over to § 112. 3. (**81**).

  b. IT BECOMES TURBID, AND DEPOSITS A PRECIPI-
TATE : CITRIC ACID.

 3. The fluid of 2. *a.* (80) is mixed with alcohol. **81**

  a. IT REMAINS PERFECTLY TRANSPARENT: absence of
malic acid. Pass over to § 112. 4. (**82**).

  b. A PRECIPITATE IS FORMED : MALIC ACID. To re-
move all doubt on this point, it is *invariably* necessary
to have recourse to the reaction with acetate of lead.
(§ 103. *e.*)

 4. A portion of the original solution is neutralized *per-* **82**
fectly (if not already absolutely neutral) either with ammonia
or with hydrochloric acid, and solution of perchloride of iron
is then added.

  a. A BULKY PRECIPITATE FORMS OF A CINNAMON OR
DIRTY YELLOW COLOR. The precipitate is washed and
afterwards heated with ammonia ; the solution is filtered
and the filtrate concentrated by evaporation ; it is then
divided into two portions, and some hydrochloric acid
added to the one : the formation of a precipitate indicates
BENZOIC ACID. The other portion is mixed with alcohol
and chloride of barium added : the formation of a precipi-
tate indicates SUCCINIC ACID. (Compare § 104. *a.* and *b.*)

  b. THE LIQUID ACQUIRES A RATHER DEEP RED TINT, **83**
AND, UPON PROTRACTED BOILING, A LIGHT REDDISH-
BROWN PRECIPITATE SEPARATES : acetic acid or formic
acid. A portion of the solid salt under examination, or,
should the substance to be analysed happen to be in the
fluid state, of the residue remaining upon the evaporation
of the liquid—(which, if acid, is first to be neutralized
with potassa)—is heated with sulphuric acid and alcohol,
(§ 105. *a.*) The characteristic odor of acetic ether, in-
dicates the presence of ACETIC ACID.

 If the operator fail to detect acetic acid in the fluid,
he may conclude that the substance under examination
contains FORMIC ACID : all doubt on this point may be
removed by the reactions with nitrate of silver and per-
chloride of mercury. (§ 105. *b.*)

*Compounds which are supposed to consist of but one acid
and one base, &c.*

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER,
BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR
AQUA REGIA.

Detection of the base. *

§ 113.   84

A portion of the solution in hydrochloric acid, nitric acid,
or aqua regia, is diluted with water, † and the further opera-
tions are conducted exactly as directed at § 110, beginning
at 1. (48) in cases where the substance is dissolved in nitric
acid, and at 2. (50) if the solution already contains hydro-
chloric acid.   I must claim particular attention of the student
to the following remark.   I have stated at § 110. 3. *b. β. cc.*
(59)that, if in cases where we have A SUBSTANCE SOLUBLE IN
WATER before us, we obtain, in the course of the examination,
a white precipitate upon testing with hydrosulphuret of am-
monia—(after having neutralized with ammonia the free acid
either originally present in, or previously added to, the solu-
tion under examination)—this precipitate can consist only
either of sulphuret of zinc, or of alumina.   But the case is
different when the substance, though INSOLUBLE IN WATER,
dissolves in hydrochloric acid ; for in that case a white pre-
cipitate produced by hydrosulphuret of ammonia, in the pre-
sence of chloride of ammonium, may consist also of a PHOS-
PHATE OF THE ALKALINE EARTHS, and likewise of OXALATE OF
LIME, BARYTA, and STRONTIA, possibly also from the presence
of a metallic fluoride,‡ or the fluoride of an alkaline earth.   If,
therefore, a white precipitate is produced upon testing an acid

* Regard has also been had to certain salts, since this course of examina-
tion leads directly to their detection.

† If upon the addition of the water, the liquid becomes turbid or deposits
a white precipitate, this indicates the presence of antimony, bismuth, or tin.
(Compare § 108. 4. (31).

‡ No further notice of the fluorides need be taken in this part of the
course, they will be referred to § 126 (at the end).

solution, under the circumstances stated, and according to the directions of § 110. 3. *b.* *β.* *cc.* (59), the following method is to be pursued. Caustic potassa in excess is added to a small portion of the original hydrochloric solution.

1. THE PRECIPITATE WHICH FORMS AT FIRST, REDISSOLVES **58** IN AN EXCESS OF THE PRECIPITANT: absence of the salts of the alkaline earths; presence of ZINC or ALUMINA; to distinguish between these, the potassa solution is tested with sulphuretted hydrogen and chloride of ammonium. (Vide supra § 110. 3. *b.* *β.* *cc.* (59). The alumina may have been present and precipitated as PHOSPHATE OF ALUMINA. This is ascertained by dissolving the precipitate in hydrochloric acid, adding tartaric acid, supersaturating with ammonia and mixing with sulphate of magnesia. If phosphoric acid is really present, a precipitate of basic phosphate of ammonia and magnesia will form upon the joint addition of these reagents, (in most cases, however, only after the lapse of some time.) The reason why the precipitates must be further tested before the presence of phosphoric acid is determined, and the method of proceeding, is explained § 99. *a.* 10.

2. THE PRECIPITATE FORMED DOES NOT REDISSOLVE IN **86** AN EXCESS OF THE PRECIPITANT: presence of a phosphate or oxalate with an alkaline earthy base. It is now necessary to ascertain by preliminary examination, whether we have an oxalate or a phosphate before us: for this purpose a portion of the original substance under examination is ignited. Should it be converted into a carbonate by this process, either with slight, or without any blackening, the salt under examination is an OXALATE, whilst if it remains unaltered upon ignition, this is a sure proof that we have a PHOSPHATE before us. Whether the compound has been transformed into a carbonate by ignition, is readily ascertained by pouring some water over the residue, and then treating it with acids, when ensuing effervescence will at once set the matter at rest, (supposing, of course, that the examined salt did not present this property previous to ignition.)

    a. THIS PRELIMINARY EXAMINATION DENOTED THE **87** PRESENCE OF A PHOSPHATE.

To a portion of the original hydrochloric solution, ammonia is added to feebly alkaline reaction, then acetic acid until the precipitate formed is redissolved, and finally solution of acetate of soda in excess; it is now tested with a very small portion (a glass rod moistened is sufficient) of a solution of perchloride of iron. The formation of a yellowish-white gelatinous precipitate (perphosphate of iron) confirms the presence of PHOSPHORIC ACID. Solution of perchloride of iron is now dropped into the same fluid until the latter appears distinctly red, owing to the formation of peracetate of iron; the mixture is then heated to boiling and maintained for some time in a state of ebullition, whereupon a ruddy brown precipitate will separate, which is then to be filtered off from the colorless fluid immediately after the ebullition has ceased. By this operation the phosphoric acid is separated from its base and precipitated in combination with peroxide of iron, and mixed with basic peracetate of iron, whilst the filtrate contains the alkaline earthy base in combination with chlorine; the precise nature of this base is finally ascertained in the usual manner. Vide 110. 4. (62).

b. THE PRELIMINARY EXAMINATION INDICATED THE **88** PRESENCE OF AN OXALATE.

Two ways are open in this case to ascertain beyond doubt the nature of the acid and base :—

1. A portion of the compound under examination is ignited, the residue dissolved in hydrochloric acid, and the solution finally tested in the usual manner for the alkaline earthy base. Another portion of the substance under examination is then tested with concentrated sulphuric acid, to remove all doubt as to the presence of oxalic acid. (§ 99. c.)

2. A portion of the compound is boiled for some time with a concentrated solution of carbonate of potassa, and the fluid then filtered off from the residue. This residue contains the alkaline earth, which forms the base of the substance under examination, in

combination with carbonic acid, whilst the filtrate con-
tains the oxalic acid in combination with potassa. The
filtrate is now acidified with acetic acid, and the pre-
sence of the oxalic acid finally proved by testing with
solution of sulphate of lime. (§ 99. c.) The residue is
thoroughly washed, subsequently dissolved in hydro-
chloric acid, and the solution treated in the usual
manner. Vide § 110. 4. **(62)**.

*Compounds which are supposed to consist of but one acid and
one base, &c.*

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN
WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID,
OR AQUA REGIA.

DETECTION OF THE ACID.

I. *Detection of inorganic acids.*

§ 114.   **89**

1. CHLORIC ACID cannot be present, since all chlorates with-
out exception are soluble in water; the nitrates also, with the
exception of a few, being soluble in water, the presence of
NITRIC ACID may usually be disregarded. The basic nitrate of
bismuth forms the most frequently occurring exception to the
general rule of the solubility of the nitrates in water. The
presence of nitric acid in *insoluble* nitrates may be most readily
recognized by the deflagration which ensues upon throwing a
sample of the compound under examination upon red-hot
charcoal. The deflagration which occurs upon fusing a nitrate
with cyanide of potassiun, is a still more conclusive test.
(Vide § 102. a.) For the analysis of those of the metallic
cyanides which are insoluble in water, I refer to § 131.

2. The course of examination which I have laid down for the **90**
detection of the bases leads likewise to that of ARSENIOUS and
ARSENIC ACIDS, CARBONIC ACID, HYDROSULPHURIC ACID, and
CHROMIC ACID. With regard to the latter acid, I repeat here
that its presence is indicated by the yellow or red color of the

compound, the evolution of chlorine which ensues upon boil-
ing with hydrochloric acid, and the subsequent discovery of
oxide of chromium in the solution. Fusion of the compound
under examination with carbonate of soda and nitrate of
potassa is, however, the most conclusive test for chromic acid.
(§ 97. *b.*)   Silica is determined as directed § 107. I. 4. *b. a.*
(22); as well as by the solution § 109. A. 2. *a.* (36).

3. A sample of the substance under examination is boiled 91
with nitric acid.

a. If nitric oxide gas is evolved,—which may be readily
recognized by the red fumes of nitrous acid forming in the
air,—this indicates the presence of a SULPHURET; whilst
the evolution of carbonic acid is indicative of a CAR-
BONATE. The positive proof of the presence of a sulphuret
may be obtained by testing the nitric solution with
chloride of barium, with which reagent it must yield a pre-
cipitate of sulphate of baryta, which even a large proportion
of water fails to dissolve. A metallic sulphuret may also
be detected with certainty according to § 101. *e.* 4 and 5.

b. If violet vapors escape, the compound may be sup-
posed to be an IODIDE. A slip of paper, covered with moist
starch, is the most conclusive test for iodine. (§ 101. *c.*)

4. A portion of the nitric acid solution (which is to be first 92
filtered, should the acid have failed to dissolve the whole of the
sample) is diluted with water, and tested with nitrate of silver.
The formation of a white precipitate, soluble in ammonia, and
fusing without decomposition when heated, indicates the
presence of CHLORINE.

5. A portion of the substance is boiled with hydrochloric 93
acid, and the solution filtered, should the acid fail to dissolve
the whole of the substance. The solution or filtrate, as the
case may be, is then diluted with water, and nitrate of baryta
added. The formation of a white precipitate, which does not
redissolve, even though a large amount of water be added to
the fluid from which it has separated, indicates the presence of
SULPHURIC ACID.

6. Test for BORACIC ACID as directed at § 111. 6. (75).

7. Should none of these acids be present, the analyst may **94**
suspect the presence of either PHOSPHORIC ACID or OXALIC
ACID, or the absence of all acids.   Were the phosphoric acid
combined with an alkaline earth, or with alumina, and the
oxalic acid with lime, baryta, or strontia, they would have
been already detected while testing for these bases. (§ 113).
The presence of these two acids is to be suspected, only if the
examination for bases has revealed the presence of other bases
than the alkaline earths.   Should this be the case, the fluid is
prepared for further examination by precipitating and separat-
ing the heavy metals from it—(this is effected in acid solutions
by means of sulphuretted hydrogen, and in alkaline solutions
by hydrosulphuret of ammonia)—and is then tested for phos-
phoric acid and oxalic acid, according to the instructions given
at § 111. 4. (**71**).

8. For the detection of BROMINE, and FLUORINE, I refer to
§ 126, (at the end).

*Compounds which are supposed to consist of but one base and
one acid, &c.*

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER,
   BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR
   AQUA REGIA.

DETECTION OF THE ACID.

II. *Detection of organic acids.*

§ 115.   **95**

1. A sample of the substance under examination is dis-
solved in the smallest possible quantity of hydrochloric acid.
If there be a residue this must be separated by filtration,
and afterwards tested for BENZOIC ACID by heating it. Car-
bonate of potassa in excess is added to the solution, and
the mixture boiled for some time, and filtered.   The alkaline
filtrate which now contains the organic acid is exactly saturated
with hydrochloric acid, and the mixture then tested, as directed

§ 112.   No regard need be had to formic acid, all the formiates being soluble in water.

2. ACETIC ACID is most readily detected in such compounds by means of sulphuric acid and alcohol. (§ 105, *a*.)

Compounds which are supposed to consist of but one acid and one base, &c. 🍴

C. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

DETECTION OF THE BASE AND THE ACID.

§ 116.   96

Under this head we have to consider, SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, SILICA, SULPHATE OF LEAD, CHLORIDE OF LEAD, and CHLORIDE OF SILVER, as the most frequently occurring compounds belonging to this class. For the less frequently occurring insoluble compounds, I refer to § 130.

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. However, as these compounds are very difficult of solution, I have included them among the class of insoluble substances, that they may be detected here, should they have been overlooked in the course of the examination of the aqueous or acid solutions of the substances to be analyzed.

1. A very minute quantity of the substance under examination is treated with hydrosulphuret of ammonia.

a. IT BECOMES BLACK ; this indicates the presence of a 97 SALT OF LEAD, or of CHLORIDE OF SILVER. A somewhat larger portion of the substance is then digested for some time with hydrosulphuret of ammonia. This effects the decomposition of the metallic salt and the formation of a sulphuret, .which latter remains undissolved, whilst we have in solution the acid of the metallic salt combined with the ammonia of the hydrosulphuret of ammonia ;

after filtration the residue is washed, dissolved in nitric acid, and tested for lead with sulphuric acid; and for silver, with hydrochloric acid, and the subsequent addition of ammonia. One portion of the filtrate is tested for SULPHURIC ACID, with chloride of barium, after having previously decomposed the excess of the hydrosulphuret of ammonia, by adding hydrochloric acid and boiling the mixture ; another portion is tested for HYDROCHLORIC ACID, with solution of nitrate of silver, after previous acidification of the liquid with nitric acid, and ebullition of the mixture.

b. IT REMAINS WHITE. Absence of a heavy metallic **98** oxide. A small portion of the very finely-powdered substance under examination is mixed with four times its quantity of carbonate of soda and potassa, the mixture introduced into a small platinum crucible, and fused over a Berzelius' spirit-lamp. The fused mass is boiled with water.

a. Complete solution ensues : SILICA. All doubt re- **99** garding the presence of this substance may be removed by supersaturating the solution with hydrochloric acid, and evaporating to dryness. This operation serves to convert the silicic acid into the insoluble modification. It will, accordingly, now remain undissolved upon treating the residue with water. If the residue be mixed with carbonate of soda, and exposed to a strong blowpipe flame, a clear bead will be produced. (§ 100, *b.*)

β. There is a white residue ; this indicates the pre- **100** sence of a SULPHATE OF THE ALKALINE EARTHS. The solution is filtered, the filtrate acidified with hydrochloric acid, diluted with water, and then tested for SULPHURIC ACID, with chloride of barium. The white residue which contains the alkaline earth in the form of a carbonate is carefully washed, dissolved in a small quantity of dilute hydrochloric acid, and the solution tested for BARYTA, STRONTIA, and LIME, according to the instructions given at § 110. 4. (**62**).

*Compounds in which all the more frequently occurring Bases,
Acids, Metals, and Metalloids, are supposed to be present.*

A. SUBSTANCES BOTH SOLUBLE AND INSOLUBLE IN WATER,
AND SOLUBLE IN HYDROCHLORIC ACID OR NITRIC ACID.

Detection of the bases.*

§ 117.   **101**

I have taken classes I. and II. (vide § 109.) together, be-
cause the systematic course, and method of examination is in
most cases the same for both. Those parts which refer only
to substances insoluble in water, but soluble in hydrochloric
acid or nitric acid, are enclosed between inverted commas
(" —— "), and may therefore be passed over unnoticed, when
examining substances, soluble in water.

I. SOLUTION IN WATER.

A small quantity of hydrochloric acid is added.

1. THE SOLUTION HAD AN ACID OR NEUTRAL REACTION **102**
PREVIOUSLY TO THE ADDITION OF THE HYDROCHLORIC ACID.

   a. NO PRECIPITATE IS FORMED : this indicates the
   absence of silver and protoxide of mercury. Pass over
   to § 118.

   b. A PRECIPITATE IS FORMED ; hydrochloric acid is
   added to the solution drop by drop, until further preci-
   pitation ceases ; about six or eight drops more of hydro-
   chloric acid are then added, the mixture shaken, and the
   fluid filtered from the precipitate, which may consist
   of chloride of silver, protochloride of mercury, chloride
   of lead, a basic salt of antimony, or possibly also of
   benzoic acid. The basic salt of antimony, however,
   redissolves in the excess of hydrochloric acid; conse-
   quently if the instructions given have been strictly fol-
   lowed, the precipitate collected upon the filter can consist
   only of chloride of silver, protochloride of mercury,

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* The arsenious and arsenic acids, and several salts, are also included here,
since this course of examination leads to their detection.

or chloride of lead,—(with benzoic acid, we have no business in this place.)

The precipitate collected upon the filter is washed twice with water, and the washings are added to the filtrate, the latter is then strictly examined according to the directions of § 118, even though the addition of the washings to the acid filtrate should produce turbidity in the fluid; (this indicates the presence of compounds of antimony, bismuth, or protoxide of tin.)

The washed precipitate is now treated as follows:

α. Hot water is poured over it, upon the filter, and **103** the fluid running off is tested with sulphuric acid for LEAD. The non-formation of a precipitate, upon the addition of the sulphuric acid, simply proves that the precipitate produced by hydrochloric acid contains no lead, and not by any means the total absence of this metal, since hydrochloric acid fails to precipitate it from very dilute solutions.

β. Solution of ammonia is now poured over the precipitate upon the filter. Should this change it to black or grey, it is a sign of the presence of PROT-OXIDE OF MERCURY.

γ. The ammoniacal fluid running off in β., is mixed with nitric acid. The formation of a white, curdy precipitate indicates the presence of SILVER. (Should the precipitate contain lead, the ammoniacal solution will generally appear turbid, owing to the separation of a basic salt of lead.)

This, however, does not interfere with the testing for silver, since the basic salt of lead redissolves upon the addition of nitric acid.

2. THE ORIGINAL AQUEOUS SOLUTION HAD AN ALKALINE REACTION.   **104**

a. THE ADDITION OF HYDROCHLORIC ACID TO STRONG-LY ACID REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON CONTINUED ADDI-

TION OF HYDROCHLORIC ACID ; pass over to § 118. The
passage in § 117, respecting bodies soluble in acids but
insoluble in water, must here be borne in mind.

b. THE ADDITION OF HYDROCHLORIC ACID TO THE
ORIGINAL SOLUTION PRODUCES A PRECIPITATE WHICH
DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECI-
PITANT, EVEN UPON BOILING.

a. The formation of the precipitate is attended 105
*neither with evolution of sulphuretted hydrogen nor
of hydrocyanic acid.* The fluid is filtered from the
precipitate, and the filtrate treated according to § 118.

aa. THE PRECIPITATE IS WHITE. It can, in that
case, consist only of CHLORIDE OF LEAD, SULPHATE
OF LEAD, or CHLORIDE OF SILVER. Test for the
bases and acids of these three compounds according
to the instructions of § 130, bearing in mind that
the chloride of lead or chloride of silver which may
be present can have been formed in the process.

bb. THE PRECIPITATE IS YELLOW OR ORANGE.
In this case it may consist of SULPHURET OF AR-
SENIC, (and if the fluid from which it separated was
not boiled long, or only with very dilute hydro-
chloric acid), also of sulphuret of antimony or bisul-
phuret of tin, which substances were originally
dissolved in solution of ammonia, borax, phosphate
of soda, or some other alkaline fluid, with the
exception of solutions of alkaline sulphurets and
cyanides. The precipitate is tested according to
§ 119.   •

β. The formation of the precipitate is attended 106
*with evolution of sulphuretted hydrogen gas, but not
of hydrocyanic acid.* *

aa. THE PRECIPITATE IS OF A PURE WHITE
color AND CONSISTS OF SEPARATED SULPHUR. In

* Should the odor of the evolved gas leave the analyst in doubt regarding
the actual presence or absence of hydrocyanic acid, he need simply add some
chromate of potassa to a sample of the fluid, previously to the addition of
the hydrochloric acid.

˙this case an alkaline sulphuret with excess of sul-
phur is present. Filter the solution and pass over
to § 121, bearing in mind that of the substances
considered in that paragraph, the heavy metals
cannot well be present.

bb. THE PRECIPITATE IS COLORED. In this
case we may conclude that a metallic sulphur salt is
present, i. e. a combination of an alkaline sulphur
base with an electro-negative sulphuret. The fluid
is filtered off from the precipitate, and the filtrate is
treated as directed in *aa.* The precipitate is treated
according to the directions given at § 118.3. (116).
It may consist of SULPHURET OF GOLD, SULPHURET
OF PLATINUM, SULPHURET OF TIN, SULPHURET OF
ARSENIC, OR SULPHURET OF ANTIMONY. It might,
however, consist entirely or partially of BISULPHURET
OF MERCURY or of SULPHURET OF COPPER, since
the former is readily soluble in sulphuret of potas-
sium, and the latter slightly soluble in sulphuret of
ammonium.

γ. *The formation of the precipitate is attended with* **107**
*evolution of hydrocyanic acid, with or without simul-
taneous disengagement of sulphuretted hydrogen.*
This indicates the presence of an ALKALINE CYANIDE,
and, if the evolution of the hydrocyanic acid is at-
tended with that of sulphuretted hydrogen, of an alka-
line SULPHURET also, in this case the precipitates may,
besides the compounds enumerated sub. α. (105) and
β. (106), contain many other substances, (e. g. sul-
phuret of nickel, cyanide of nickel, cyanide of silver,
&c.) The mixture is kept boiling (with further ad-
dition of hydrochloric acid) until the whole of the hydro-
cyanic acid is expelled ; the solution, or, should there be
any residue, the filtrate is treated according to § 118;
and the residue (if any) is treated according to § 130.

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO **108**
PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES
EVOLUTION OF GAS.

α. *The escaping gas smells of sulphuretted hydro-*

gen; this indicates a SIMPLE ALKALINE SULPHUR COMPOUND. The further operations are conducted as directed at *b. β. aa.* (106).

β. *The escaping gas is inodorous;* in this case it is carbonic acid which was combined with an alkali. Pass over to § 118.

γ. *The escaping gas smells of hydrocyanic acid* (no matter whether sulphuretted hydrogen or carbonic acid are evolved at the same time or not.) This indicates the presence of an ALKALINE CYANIDE. The mixture is kept boiling until the whole of the hydrocyanic acid is expelled, and then treated according to the instructions which will be found at § 118.

II. SOLUTIONS IN HYDROCHLORIC ACID.

These are treated as § 118 directs.

III. SOLUTIONS IN NITRIC ACID.

A small portion of the solution is diluted with much water.

1. IT REMAINS TRANSPARENT: add hydrochloric acid.   **109**

a. No precipitate is formed. Absence of silver. The original solution is treated according to § 118.

b. A precipitate is formed. If this does not redissolve upon heating the fluid, but is, after being thoroughly washed, dissolved by ammonia, SILVER is present. The original solution is treated as directed at § 118.

2. THE SOLUTION BECOMES MILKY: BISMUTH OR ANTIMONY. The fluid is filtered, and the filtrate tested for silver according to the directions of § 117. III. 1. (**109**); the original solution is treated as § 118 directs.

§ 118.

SOLUTION OF SULPHURETTED HYDROGEN IS ADDED TO A **110** SMALL PORTION OF THE CLEAR ACID SOLUTION, UNTIL THE FLUID, WHEN AGITATED, EMITS A DISTINCTLY PERCEPTIBLE

ODOR OF SULPHURETTED HYDROGEN ; A GENTLE HEAT IS THEN
APPLIED.

    a. NO PRECIPITATE IS FORMED, even after the lapse
of some time. Pass over to § 121, for neither lead,
bismuth, cadmium, copper, mercury, gold, platinum,
antimony, tin, nor arsenic,* are present ;† the absence
of peroxide of iron and of chromic acid is also indi-
cated by this negative reaction.

    b. A PRECIPITATE IS FORMED.

      aa. The precipitate is of a pure white color, slight **111**
and pulverulent, and does not redissolve on addition
of hydrochloric acid. It consists of separated sulphur,
and indicates the presence of PEROXIDE OF IRON ‡
None of the other metals, enumerated at § 118. *a.*
can be present. The original solution is treated as
§ 121 directs.

      bb. The precipitate is colored.   **112**
Solution of sulphuretted hydrogen is added to the
larger portion of the acid or acidified solution, until
the latter smells distinctly of this gas, and the preci-
pitate ceases to increase upon continued addition of
the reagent ; the mixture is then gently heated, and
agitated for some time.

    * Should the preliminary examination have led the analyst to suspect the
presence of arsenic acid, he ought now to endeavour to obtain the most con-
clusive evidence of the absence of this acid ; this may be effected by allowing
the sample to stand for some time in warm water, or by treating it with
sulphurous acid previous to the addition of the sulphuretted hydrogen.
(Compare § 95, *e.*)

    † In solutions containing much free acid, the precipitates are frequently
formed only after dilution with water.

    ‡ Sulphur will precipitate also if sulphurous acid, iodic acid, or bro-
mic acid, are present, (these substances do not come within the scope of the
present work), and also if chromic acid, chloric acid, or free chlorine are pre-
sent. In presence of chromic acid, the separation of the sulphur is attended
with reduction of the acid to oxide of chromium, in consequence of which the
reddish-yellow color of the solution changes to green. (Compare § 97. *b.* 3.)
The white sulphur suspended in the solution, appears at first like a green
precipitate, which frequently tends to mislead novices.

In some cases, and more particularly when there is any reason to suspect the presence of arsenic, it will be found more convenient to transmit sulphuretted hydrogen gas through the diluted solution, instead of adding sulphuretted hydrogen water.   .

1. THE PRECIPITATE IS OF A PURE YELLOW COLOR. In **113** this case it can consist only of ARSENIOÜS or ARSENIC ACID, of PEROXIDE OF TIN, or of OXIDE OF CADMIUM. The fluid— which is afterwards to be tested according to § 121—is separated from the precipitate,* the latter washed, and a small portion of it digested with ammonia.

a. The precipitate is completely redissolved : absence of cadmium. The rest of the precipitate is tested for TIN and ARSENIC, according to the directions of § 119. 1. **(120)**.

b. There is a yellow residue even after addition of a fur- **114** *ther amount of ammonia and application of a moderate heat ;* CADMIUM. The whole of the precipitate is treated like the sample, and the fluid filtered from the undis-solved residue ; hydrochloric acid in excess is added to the filtrate. The non-formation of a precipitate denotes that the first precipitate consisted exclusively of sul-phuret of cadmium ; but if one be formed, it may consist of PEROXIDE OF TIN or ARSENIC, and is to be examined according to § 119. 1. **(120)**.

2. THE PRECIPITATE IS ORANGE RED, OR YELLOW, WITH A **115** SHADE OF ORANGE. It indicates ANTIMONY, ARSENIC or CAD-MIUM, but may, moreover, contain TIN—(should this metal have been present as peroxide—the precipitate is separated from the fluid—(which is subsequently tested as § 121 directs)—washed, and a small portion of it digested with hydrosulphuret of ammonia containing an excess of sulphur.

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* The best way of separating a precipitate from a fluid, and which ought to be pursued in qualitative analysis, whenever practicable, is to allow the precipitate to subside. This may almost invariably be effected by the appli-cation of heat and a vigorous shake of the fluid)—and to transfer the fluid alone to the filter, leaving the precipitate in the test tube, where it may then be washed by decantation.

a. It redissolves completely: absence of cadmium. The rest of the precipitate is treated as directed at § 119. 2. **(123)**.

b. There is a yellow residue, even after protracted digestion, with a larger quantity of hydrosulphuret of ammonia: CADMIUM. The entire precipitate is then treated in the same manner as the sample, and the fluid is filtered from the sulphuret of cadmium ; a slight excess of hydrochloric acid is added to the filtrate, and the precipitate formed is treated as directed at § 119.2. **(123)**.

3. THE PRECIPITATE IS OF A DARK BROWN OR BLACK COLOR. **116** It is separated from the fluid—(which is afterwards tested according to the directions of § 121)—washed with water, and a small portion of it is then digested for some time, with hydrosulphuret of ammonia, containing an excess of sulphur.*

a. The precipitate redissolves completely in hydrosul- **117** *phuret of ammonia (or sulphuret of potassium) ;* absence of cadmium, lead, bismuth, copper, and mercury : § 120 may therefore be passed over. The rest of the original precipitate is treated according to the instructions of § 119.

b. The precipitate is not redissolved, or at least not **118** *completely.* The mixture is diluted with from four to

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* If the solution contain copper, which is generally revealed by the color of the fluid, and may be ascertained positively by testing with a clean iron rod, (vide § 92. *b.* 8.) solution of sulphuret of potassium is to be substituted for hydrosulphuret of ammonia, and the mixture is boiled, (vide § 92. *b.* 3.) But if the fluid, besides copper, contain also peroxide of mercury (the presence of which is generally sufficiently revealed by the several changes of color exhibited by the precipitate forming upon the addition of the sulphuretted hydrogen, (§ 92. *a.* 3.) and which, in doubtful cases, may be ascertained by testing a sample of the original acidified solution, with protochloride of tin), hydrosulphuret of ammonia must be used, although the separation of the sulphuret of the antimony group from the sulphuret of copper is not fully effected in such cases ; since were sulphuret of potassium used, the bisulphuret of mercury would dissolve in this reagent, and this would impede the further examination of the sulphurets of the antimony group.

five parts of water, the fluid is then filtered from the precipitate, and hydrochloric acid in excess added to the filtrate.

    a. The fluid turns milky, owing to the separation of sulphur. Absence of gold, platinum, tin, antimony, and arsenic. The rest of the original precipitate is treated according to the directions of § 120.

    β. A colored precipitate is formed. The color of **119** which is minutely inspected; the rest of the original precipitate is then treated like the sample, i. e. digested with hydrosulphuret of ammonia containing an excess of sulphur, or with sulphuret of potassium, as the case may be; the undissolved residue is allowed to subside, and the supernatant fluid is passed through the filter; the residue in the test-glass is once more digested with yellow hydrosulphuret of ammonia (respect. sulphuret of potassium), and the fluid filtered from the residue,* which latter is then washed and kept for further examination, according to the direction of § 120. The whole of the filtrate is diluted with water, and a slight excess of hydrochloric acid added to the fluid; the mixture is now heated and the precipitate produced is treated as follows: (§ 119).

<div style="text-align:center">§ 119.</div>

THE PRECIPITATE PRODUCED BY HYDROCHLORIC ACID (§ 118. 3. *b. β.*) **(119.)** IS :

    1. OF A PURE YELLOW COLOR WITHOUT THE SLIGHTEST **120** SHADE OF ORANGE : ARSENIC OR TIN. The fluid is filtered

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    * Should the residue readily subside, it is to be left in the test-glass, and washed by decantation. But if its subsidence proceeds slowly and with difficulty, it is to be transferred to and washed upon the filter; a hole is then made in the bottom of the filter, and the residue is washed into a small porcelain basin; the application of a gentle heat will now materially aid the subsidence of the residue, and the separated water may then be d▪▪▪ted.

from the precipitate, which is then thoroughly washed ; a
small portion of the washed precipitate is afterwards heated
upon the lid of a porcelain crucible, or a broken piece of
porcelain or glass.

    a. Complete volatilization ensues : absence of tin. **121**
The rest of the precipitate is carefully dried and mixed
with about six times its weight of a perfectly dry mix-
ture of equal parts of carbonate of soda and cyanide of
potassium ; the whole mass is introduced into a small
glass tube expanded into a bulb at one end ; the heat of
a BERZELIUS lamp is then applied. The formation of a
metallic mirror is a positive proof of the presence of
ARSENIC. Should the amount of the precipitate be very
minute, the reduction is to be effected in a slow stream
of carbonic acid gas (compare § 95. *d.* 10). Whether
the arsenic was present in the form of arsenious acid or
in that of arsenic acid, the analyst may ascertain by the
method described at the end of § 95.

    b. There is a fixed residue. Probable presence of **122**
tin. The rest of the precipitate is thoroughly dried
upon the filter, and mixed with about equal parts of
effloresced soda and nitrate of soda ; the mixture is
projected in small portions into a small porcelain cruci-
ble containing two parts of nitrate of soda in a state of
fusion.*

    The fusing mass is poured upon a broken piece of por-
celain, (to preserve the crucible,) and allowed to cool ;
when cold, it is reduced to powder, and digested with cold
water ; the fluid is filtered from the white residue, (which

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  * Should the amount of the precipitate be so minute that this operation
cannot be conveniently performed, the dry filter, with the precipitate adhering
to it, is to be cut into small fragments, which are then to be rubbed together
with some carbonate of soda and nitrate of soda, the whole mass (the paper
as well as the powder) being then projected into the fusing nitrate of soda.
It is preferable, however, in such cases, to procure a sufficiently large amount
of the precipitate, or there will be but little hope of effecting the positive
detection of the tin.

will remain if tin is really present,) and this is tho-
roughly washed ; the presence of tin is then finally
demonstrated by reducing the washed residue before
the blow-pipe with cyanide of potassium, and carbonate
of soda, and rubbing the reduced mass with strong
pressure in a small mortar, with some water. (Vide
§ 95. c. 7). Or if the quantity be but small, it is to
be dissolved in hydrochloric acid, precipitated with sul-
phuretted hydrogen, and warmed. (§ 95. c. 3.) Whe-
ther the tin was present as PROTOXIDE, the analyst may
ascertain by mixing a small sample of the original
aqueous or hydrochloric solution, with a drop of nitric
acid and some perchloride of gold. (§ 95. b. 6.)

The filtrate is divided into two portions, and highly
dilute nitric acid is added cautiously to the one to feebly
acid reaction, and heat applied.* Nitrate of silver is
then added, and the fluid filtered ; should any chloride
of silver separate, (which will invariably happen in
cases where the reagents were not perfectly pure, or
the precipitate has not been thoroughly washed,) a
layer of very dilute solution of ammonia (20 parts of
water to one part of common ammonia) is gently poured
upon the filtrate, the tube being held in an oblique
position for this purpose, so that the solution of am-
monia may run down the side; the mixture is then al-
lowed to stand at rest for some time. The formation
of a reddish-brown precipitate, which appears hovering
cloud-like between the two layers, (and may be seen far
more readily and distinctly by reflected than by trans-
mitted light,) denotes the presence of ARSENIC. To
gain more positive information on this point, the se-

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* In some cases where a rather larger proportion of carbonate of soda has
been used, a trifling precipitate (hydrated peroxide of tin) will separate upon
the acidification of the filtrate with nitric acid. This may be filtered off and
tested for tin in the same manner as the undissolved residue, but if the pre-
sence of tin has been already demonstrated, this precipitate may be altogether
disregarded, and the operation proceeded with as directed above.

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cond portion of the filtrate (of the solution of the defla-
grated mass) is precipitated with solution of neutral
acetate of lead; the precipitate is thrown on a filter, dried
between blotting-paper, and subsequently exposed on
charcoal to the inner blow-pipe flame.   If arsenic is
really present, a globule of metallic lead containing an
admixture of arsenic will be produced, which will emit
the odor of garlic for a long time, when exposed to the
reducing blow-pipe flame.   The only *positive proof* of
the presence of arsenic, however, is the exhibition of
this substance in the metallic state.   (Compare § 95. *d.*
and *e.*)   Whether the arsenic was present in the form of
arsenious acid, or in that of arsenic acid, the analyst
may ascertain by the method described at the end of
§ 95.

2. Orange-red, or yellow approaching to orange, ANTI- **123**
MONY; besides which tin and arsenic may be present.   The
well-washed precipitate is dried, rubbed up with equal por-
tions of carbonate and nitrate of soda, and the mixture
gradually added to two parts of fused nitrate of soda in a
porcelain crucible or dish.   The cooled mass is now softened
with cold water, thrown on a filter, and the white residue
(which contains the antimony as antimoniate of soda, and at
the same time some tin as peroxide) well washed with a mix-
ture of one volume of water, and two of alcohol.   These
washings are not to be mixed with the filtrate.

The filtrate must be carefully tested for arsenic, according
to the method given, § 119. 1. *b.* (**122**).*   The residue is **124**
now boiled with concentrated solution of potassa, or soda.
After a short time add an equal quantity of alcohol, and
allow it to stand half an hour, then filter.   Under these

* Should a precipitate (hydrated antimonic acid, or hydrated peroxide of
tin) form upon the acidification of the fluid filtered from the residue remain-
ing upon the extraction of the deflagrated mass with water, this may be
filtered off and added to the residue. However, as the latter usually contains
sufficient tin and antimony, this precipitate may be altogether disregarded,
and the process may at once proceed as directed at 119. 1. *b.* (**122.**)

circumstances the antimoniate of soda remains undissolved, whilst nearly all the oxide of tin is found in the solution.

In a very exact experiment the solution must be filtered, and the residue washed with a mixture of equal volumes of alcohol and water. The filtrate and wash-liquor, which must be kept separate, are now to be tested.

    a. The alkaline filtrate is acidified with hydrochloric **125** acid, decomposed with sulphuretted hydrogen, and warmed. A yellow precipitate indicates tin. To decide whether it existed in the original solution as proto or peroxide, proceed as directed in § 119. 1. *b.* (**122**). As a further proof, the precipitate of sulphuret of tin may be reduced before the blow-pipe to the metallic state, with soda and cyanide of potassium.

    b. The insoluble residue is to be dissolved in hydro- **126** chloric acid, some tartaric acid having been previously added, the solution decomposed with sulphuretted hydrogen and warmed. An orange-yellow precipitate denotes antimony.

3. BROWNISH-BLACK, GOLD or PLATINUM; and, besides **127** these, possibly also ANTIMONY, ARSENIC, or TIN. Add to the original solution of the substance ;

    a. Protochloride of tin ; the formation of a reddish-brown or purple-colored precipitate denotes GOLD. The presence of this metal may be positively demonstrated by testing a portion of the original solution of the substance with protosulphate of iron, since this will separate metallic gold in the form of a black powder.

    b. Chloride of ammonium ; the formation of a yellow **128** precipitate is indicative of the presence of PLATINUM. Should the solution be highly dilute, it is to be concentrated by evaporation, previously to the addition of the reagent.

A portion of the precipitate is tested for ARSENIC, ANTIMONY, and TIN, as directed at § 119. 2. (**123**.)

§ 120.

THE PRECIPITATE WHICH HAS NOT BEEN DISSOLVED BY **129** HYDROSULPHURET OF AMMONIA, or sulphuret of potassium (§ 118. 3. *b*.) **(118.)** IS WASHED, AND THEN BOILED WITH NITRIC ACID. This operation is best performed in a small porcelain basin; the boiling mass must be constantly stirred during the process.

1. THE PRECIPITATE DISSOLVES, AND NOTHING REMAINS **130** FLOATING IN THE FLUID EXCEPT THE SEPARATED, LIGHT FLOCCULENT, YELLOW SULPHUR; this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH, may be present.

If the original precipitate was a bright yellow, only cadmium is present; but if it was black or brown, the solution must be filtered from the sulphur it contains; and should much free nitric acid be present, the greater part of it must be driven off by evaporation; then proceed as follows:—First treat it with a moderate quantity of dilute sulphuric acid and warm;

a. It gives no precipitate; the absence of lead is determined; it must now be treated with excess of ammonia and warmed.

α. No precipitate; absence of bismuth. If, on the **131** addition of the ammonia, the liquid assumes a blue color, copper is present; if, however, the quantity of this metal be but small, it may in this case be readily overlooked, from the faintness of the color; it is, therefore, better to take the ammoniacal liquor which has still to be tested for cadmium, evaporate nearly to dryness, add a little hydrochloric acid, and, if necessary, a small quantity of water, then test.

aa. A few drops of the solution give, with ferro-cyanide of potassium, on a watch-glass, either a brownish-red precipitate or turbidness. Copper is present; in the latter case only in minute quantity.

bb. The remainder of the solution is decomposed

by an excess of carbonate of ammonia, warmed, and
allowed to stand for some time.   If a whitish
precipitate is formed, and this may be readily seen
even in a dark blue liquid, the presence of cad-
mium is indicated, and may be further proved by
washing the precipitate, dissolving in hydrochloric
acid, and testing with sulphuretted hydrogen, which
should cause a yellow precipitate.

β. A precipitate; bismuth is present. The solu- **132**
tion is filtered and tested for copper and cadmium
according to § 120. 1. *a. a.* (**131.**)   To test the preci-
pitate more fully for bismuth, press the filter contain-
ing it between blotting-paper, and dissolve whilst still
moist with the smallest possible quantity of hydro-
chloric acid in a watch-glass; if now the addition of
not too small a quantity of water causes a milkiness,
the presence of bismuth is confirmed.

b. A precipitate is formed; lead is present. Filter, **133**
and proceed to test the filtrate for bismuth, copper, and
cadmium, according to § 120. 1. *a.* (**130.**)*

2. THE BOILING NITRIC ACID FAILS TO REDISSOLVE THE **134**
WHOLE OF THE PRECIPITATED SULPHURETS, AND LEAVES A
RESIDUE, BESIDES THE LIGHT FLAKES OF SULPHUR THAT
FLOAT IN THE FLUID. Probable presence of PEROXIDE OF
MERCURY, (which may be pronounced as almost certain, if
the precipitate is heavy and black.)   The precipitate is al-
lowed to subside, and the fluid is filtered from it; the filtrate
is to be tested for CADMIUM, COPPER, LEAD, and BISMUTH :
a small portion of it is mixed with a large amount of solu-
tion of sulphuretted hydrogen, and, should a precipitate form,
the remainder is treated according to the directions of § 120.
1. (**130.**)   The residue is washed, dissolved by the addition of
a few drops of aqua regia, and ammonia added until the solu-
tion retains only a feebly acid reaction; a drop of the fluid is

* For another method of distinguishing cadmium, copper, lead, and bis-
muth from each other, I refer to Chapter II. (additions and remarks to
§ 120).

then placed upon a clean copper plate. If MERCURY be present, the surface of the copper will, after the lapse of some time, exhibit a white stain, which presents a metallic lustre when rubbed, and disappears upon heating. Or the solution in aqua regia is evaporated nearly to dryness, some hydrochloric acid being occasionally added; the residuary mass is diluted with water, and protochloride of tin added. The formation of a precipitate, which appears white at first, but changes to grey upon the addition of an excess of protochloride of tin, is a positive proof of the presence of mercury.

§ 121.

A SAMPLE OF THE FLUID IN WHICH SOLUTION OF SUL- **135** PHURETTED HYDROGEN HAS FAILED TO PRODUCE A PRECIPITATE, (§ 118. *a.*) OR OF THE FLUID WHICH HAS BEEN FILTERED OFF FROM THE PRECIPITATE FORMED, IS MIXED WITH AMMONIA TO ALKALINE REACTION, AND HYDROSULPHURET OF AMMONIA ADDED, (whether the ammonia has produced a precipitate or not).

In cases where but a minute quantity of hydrochloric acid is present, and therefore but little chloride of ammonium has been formed, a certain amount of solution of chloride of ammonium is to be added to the fluid, previously to the addition of the ammonia and hydrosulphuret of ammonia.

    a. No PRECIPITATE IS FORMED. Pass over to § 122, **136** for neither iron, manganese, cobalt, zinc, nickel, oxide of chromium, nor alumina, are present; nor are the phosphates of the alkaline earths, nor oxalate of lime, baryta, and strontia; nor fluorides of the metals and alkaline earths.*

    b. A PRECIPITATE IS FORMED. The whole fluid is treated in the same manner as the sample.

1. The precipitate is white; absence of iron, cobalt, and **137** nickel. All the metals and compounds mentioned in § 121, *a.* **(136)**, must be searched for, as from the light color of sul-

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* In order to simplify the following course, no notice is taken of the fluorides, or oxalates of the alkaline earths.

phuret of manganese and oxide of chromium they will not be perceptable in a large quantity of a white precipitate. Filter, and set aside the filtrate for testing according to § 122; wash the precipitate, dissolve it in hydrochloric acid, neutralize with carbonate of soda, add an excess of solution of caustic soda, and boil.

a. The precipitate formed is entirely dissolved in the **138** excess of caustic soda; absence of the phosphates of the alkaline earths, manganese, and chromium; presence of alumina (probably phosphate) or oxide of zinc. A small portion of the alkaline fluid is tested with solution of sulphuretted hydrogen for zinc; the remainder is then acidified with hydrochloric acid, and excess of ammonia added; a white precipitate indicates alumina. To prove whether it be combined with phosphoric acid, either proceed according to the method given in § 99. *a.* 10., or, what is simpler, more sensitive, and sure, test it by means of molybdate of ammonia.* The alumina to be tested for phosphoric acid is to be dissolved in hydrochloric acid, a small quantity of the solution of molybdate of ammonia added, and the mixture boiled. If the least trace of phosphoric acid is present, the liquid acquires a deep yellow color inclining to green, which disappears entirely or partially on cooling.

b. The precipitate is insoluble, or not entirely soluble, **139** in excess of solution of caustic soda. Filter; test the filtrate according to *a.* for oxide of zinc and alumina, especially the latter, combined with phosphoric acid. The precipitate is treated thus :—

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* The use of molybdate of ammonia, as a means of detecting phosphoric acid in its compounds, is a recent discovery, and it will soon become one of our most useful reagents. To prepare it, the native sulphuret of molybdenum is to be roasted in a hessian crucible placed in an inclined position, at first with a strong and afterwards with a gentler heat, until it appears yellow whilst hot and white on cooling. The molybdic acid thus obtained is ground to a fine powder, digested with caustic ammonia, and when dissolved furnishes the above-mentioned reagent.

a. A portion is tested before the blowpipe with soda for manganese, § 89. *b.* 6.

β. A second portion is fused with soda and nitrate of potassa or soda for chromium, § 88. *b.* 5, if the original solution was green, yellow, or red.

γ. The remainder is dissolved in the smallest quantity of hydrochloric acid necessary,* (if too much acid is added it must be nearly neutralized by carbonate of soda,) then treated with excess of solution of acetate of soda, and, lastly, add the smallest possible portion of perchloride of iron.

   aa. The solution remains clear; absence of phos- **140** phoric acid. The remainder of the liquid,† after adding a slight excess of ammonia, is mixed with the filtrate from the hydrosulphuret of ammonia precipitate and then examined according to § 122. If oxide of chromium is present it must be filtered off after the addition of the ammonia, and the precipitate tested as before directed: the same must be done with manganese, which, if present, gives a precipitate on adding hydrosulphuret of ammonia.

   bb. A yellowish-white flaky precipitate ; phos- **141** phoric acid ; perchloride of iron is added until the liquid (from the formation of peracetate of iron) becomes slightly red ; boil and filter off the phosphate of iron which is mixed with basic acetate of iron ; then, after precipitating the manganese (in case any be present) with ammonia and hydrosulphuret of ammonia, test the filtrate for the alkaline

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  * That the molybdate of ammonia may be used here with advantage, for the detection of phosphoric acid need not be repeated.

  † The solution may easily contain a small quantity of the alkaline earths if phosphoric and oxalic acids, &c. are not present ; whilst a portion of magnesia (and if only a trace of it be present, frequently the whole) is precipitated with the alumina ; and owing to the action of the carbonic acid of the air, traces of the other alkaline earths may possibly be found in the hydrosulphuret of ammonia precipitate.

earths with which the phosphoric acid was previously combined.

2. The precipitate caused by hydrosulphuret of ammonia 142 is not white; it may be chromium, manganese, iron, cobalt, or nickel. It is black, or approaching that color; one of the three last-mentioned metals is sure to be present. Under all circumstances, metals and compounds mentioned in § 121. *a.* (136) must be looked for. First, filter, reserving the filtrate for further examination according to § 122; then carefully wash the precipitate with water containing a little hydrosulphuret of ammonia, and afterwards drench it with dilute hydrochloric acid.

a It is entirely soluble excepting a little sulphur 143 which is separated; probable absence of cobalt and nickel. Filter, if it be necessary, then boil until all the sulphuretted hydrogen has entirely escaped, neutralize with carbonate of soda, and add some solution of soda (free from alumina) in excess; then boil, and filter off any precipitate which may remain undissolved; wash it, and proceed first to test the solution, afterwards the precipitate.

a. A little of the solution is tested with sulphuret- 144 ted hydrogen for zinc. The remainder, after acidifying with hydrochloric acid and boiling with a little chlorate of potassa, is tested with ammonia for alumina. Whether the alumina, in case any be present, is combined with phosphoric acid, decide according to § 121. 1. *a.* (138.)

β. Before examining the precipitate the following 145 question must be decided :—Was the original solution green, yellow, violet, or red; and, consequently, do any grounds exist for suspecting the presence of chromium? According to circumstances, follow either *aa.* or *bb.*

aa. There is no reason to suspect that chromium 146 exists in the precipitate.

A small portion is now tested in the outer blow-

pipe flame with carbonate of soda for manganese ;
the remainder is dissolved in hydrochloric acid ;
a little of the solution is boiled with a drop of
nitric acid, and tested with sulphocyanide or ferro-
cyanide of potassium for iron. The remainder of
the solution (if of a yellow color from chloride of
iron) is to be heated with sulphite of soda until
complete decolorization (reduction) ensues; then
nearly neutralize with carbonate of soda, and add
some acetate of soda with a little perchloride of
iron.

    aa. It forms no precipitate; absence of phos- **147**
phoric acid. The analysis of the precipitate is
now finished, unless very great accuracy is neces-
sary ; in which case we must still look for traces
of cobalt, nickel, and zinc, as well as a little mag-
nesia, which may have been thrown down with
the hydrosulphuret of ammonia precipitate.

For this end boil the remainder of the solution
with nitric acid, nearly saturate it with carbonate
of soda, and add excess of carbonate of baryta,
allowing it to digest some time with a gentle heat
and frequent agitation. Then filter off the pre-
cipitate, containing all the iron, and precipitate
the baryta with sulphuric acid ; filter, super-
saturate with ammonia, and test a small quantity
with hydrosulphuret of ammonia ; should this
cause a precipitate, treat the whole of the solu-
tion with it and filter ; then test the filtrate with
phosphate of soda for magnesia. The preci-
pitate caused by hydrosulphuret of ammonia is
to be treated with very dilute hydrochloric acid,
and if this leaves no black residue it is entirely
free from cobalt and nickel ; should a portion
remain insoluble, it is to be examined according
to § 121. 2. *b.* **(150.)** The hydrochloric acid
solution, which contains all the manganese, and

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may also contain a trace of zinc, is now boiled
with excess of caustic soda and the insoluble
portion examined before the blow-pipe for man-
ganese (supposing that it has not been previously
detected); the addition of sulphuretted hydrogen
water to the alkaline solution decides as to the
presence of zinc.

ββ. A precipitate is formed; phosphoric acid. **148**
Perchloride of iron is added until the solution
becomes slightly red; then boil and filter from
the precipitate, which contains all the phosphoric
acid; after the addition of ammonia, precipitate
with hydrosulphuret of ammonia, filter and test
the filtrate for the alkaline earths with which the
phosphoric acid existed in combination, according
to § 122. The slight precipitate caused by the
hydrosulphuret of ammonia (which contains all
the iron that existed in the solutions boiled with
acetate of soda, as protoxide, together with all
the manganese and possibly a trace of cobalt,
nickel, and zinc), must, if a very exact analysis
is required, be treated according to (**147**); that
is, first warm it with hydrochloric acid, then boil
it with nitric acid, and after nearly neutralizing
the solution with carbonate of soda, precipitate
the iron with carbonate of baryta in excess.

bb. The presence of chromium is to be suspected. **149**
In this case the precipitate is triturated with one part
of soda and three parts of nitrate of potassa or nitrate
of soda, and fused in a porcelain crucible; after cool-
ing, the mass is boiled with water and filtered. The
insoluble portion is well washed and tested according
to *aa* (**146.**) The yellow color of the solution indi-
cates the presence of chromium, which is further
proved by acidifying with acetic acid, and adding
solution of acetate of lead, § 97. *b*. 7.

b. Not entirely soluble in it, but leaves a blackish **150**

residue; presence of cobalt and nickel; well wash and test the filtrate according to *a*. (143.) Treat the precipitate as follows:—a small portion heated with borax in the inner blow-pipe flame, gives a blue bead, cobalt.

β. The remainder of the precipitate is dissolved in aqua regia evaporated almost to dryness, and cyanide of potassium, added in excess; then, after boiling some time, treat it with just sufficient dilute sulphuric acid. A whitish precipitate of cyanide or cobalti-cyanide of nickel, § 89 (and remarks) indicates nickel.

§ 122.

A PORTION OF THE FLUID IN WHICH HYDROSULPHURET **151** OF AMMONIA HAS FAILED TO PRODUCE A PRECIPITATE, OR OF THE FLUID FILTERED OFF FROM THE PRECIPITATED SUL-PHURETS, IS MIXED WITH PHOSPHATE OF SODA, AMMONIA ADDED (SHOULD THE FLUID NOT ALREADY CONTAIN FREE AMMONIA), AND THE MIXTURE WELL AGITATED.

a. No precipitate is formed : absence of the alkaline earths. Another sample of the fluid is evaporated to dryness, and the residue ignited; should it volatilize completely, neither potassa, nor soda are present : pass over to § 125. Should there be a residue, the rest of the fluid is to be evaporated to dryness, ignited, and treated according to the directions of § 124.

b. A precipitate is formed.   **152**

The remainder of the fluid is mixed with chloride of ammonium, should this salt not be present already,) and a mixture of carbonate of ammonia with some caustic ammonia added ; the whole mixture is then gently heated for some time (but not to ebullition).

1. *No precipitate is formed.* Pass over to § 123, for neither lime, baryta, nor strontia are present.

2. *A precipitate is formed.* Presence of LIME, BARYTA, or **153** STRONTIA. The fluid is filtered off from the precipitate, and the filtrate kept for further examination, according to the

directions of § 123. The precipitate is dissolved in the least possible amount of highly dilute hydrochloric acid, and the solution treated as follows:

a. Solution of sulphate of lime is added to a portion of it.

a. *No precipitate is formed,* EVEN AFTER THE LAPSE OF A CONSIDERABLE TIME. Pass over to § 122. 2. *b.* (156), for neither baryta nor strontia are present.

β. A precipitate is formed.

aa. It is formed immediately upon addition 154 of the solution of sulphate of lime : this indicates BARYTA. Besides this substance, strontia and lime may be present.

A portion of the hydrochloric acid solution of the precipitate caused by carbonate of ammonia, is evaporated to dryness, and the residue digested with absolute, or at all events very strong alcohol; filter, and heat the filtrate to the boiling point in a small dish, ignite and stir well. A carmine red-colored flame indicates strontia. When all the alcohol has burnt, some very dilute sulphuric acid is added to the contents of the crucible to precipitate the last trace of baryta, and a little strontia that may be present; after standing half an hour, it must be filtered, and the filtrate tested with ammonia and oxalate of ammonia for lime.

bb. A precipitate is formed only after some time. 155 Absence of baryta, but it contains strontia. The remainder of the hydrochloric acid solution is decomposed with dilute sulphuric acid ; after standing some time, it is filtered, and the filtrate tested with carbonate of ammonia for lime.

b. To another portion of the hydrochloric acid solu- 156 tion, add ammonia until it gives an alkaline reaction, then oxalate of ammonia; a white precipitate ; lime.

§ 123.

TAKE TWO SMALL PORTIONS OF THE FLUID IN WHICH
CARBONATE OF AMMONIA HAS FAILED TO PRODUCE A PRE-
CIPITATE, OR OF THAT WHICH HAS BEEN FILTERED FROM
THE PRECIPITATE FORMED, (§ 122. 1. (152) AND ADD
SOME SULPHATE OF POTASSA OR DILUTE SULPHURIC ACID TO
THE ONE, AND OXALATE OF AMMONIA TO THE OTHER.

1. BOTH THESE REAGENTS FAIL TO PRODUCE ANY **157**
FURTHER PRECIPITATE. This is a positive proof that the
baryta, strontia and lime, have been completely precipitated
by the carbonate of ammonia. Phosphate of soda is added
to a third portion of the fluid, (§ 122. 1.) and the mixture
stirred with a glass rod. The formation of a crystalline pre-
cipitate, (compare § 87. d. 7.) demonstrates the presence of
MAGNESIA. Whether magnesia has been detected or not,
the rest of the fluid (§ 122. 1.) is evaporated to dryness, and
the residue heated till all the ammoniacal salts are completely
expelled. Should there be no residue, pass over to § 125;
if a residue, pass over to § 124.

2. ONE OR BOTH OF THE REAGENTS STILL PRODUCE A **158**
PRECIPITATE. In that case the carbonate of ammonia has
not completely removed the whole of the baryta, strontia, and
lime. This reagent, mixed with caustic ammonia, is therefore
once more added to the rest of the fluid, and the mixture
heated for some time. The precipitate which now forms, is
filtered off, and the filtrate treated as at 1. (157.)

§ 124.

We come now to the examination for fixed alkalies and am- **159**
monia.

The compounds of the former are, with very few exceptions,
soluble in water. Therefore substances insoluble in water
need not usually be tested for the fixed alkalies.

In the case of substances insoluble in water, but soluble
in hydrochloric acid, or in nitric acid, the remainder of the
fluid in the sample of which phosphate of soda failed to pro-

duce a precipitate, (§ 122. *a.* (151)—or the solution in which carbonate of ammonia has either produced no precipitate (§ 122. *b.* 1. (152), or if one was thrown down (153), the filtrate should be kept for examination for phosphoric acid and oxalic acid. . See § 128. 8.)

The presence of magnesia renders certain modifications necessary in the method of examining for. potassa and soda ; we have therefore to distinguish two cases, viz.

1. MAGNESIA IS NOT PRESENT.   The ignited residue **160** (§ 122. *a.* (151) or § 123. 1. (157), is dissolved in a small quantity of water, alcohol added to the solution, and the alcoholic mixture heated to boiling, and kindled.

    a. THE FLAME IS VIOLET. Absence of soda ; probable presence of POTASSA.

    b. THE FLAME IS YELLOW; presence of SODA. The solution is evaporated to dryness, and the blow-pipe and test with antimoniate of potassa are resorted to as conclusive proofs of the presence of soda.   (Vide § 86. *b.*) To demonstrate the presence of potassa, the residue is dissolved in water, or, better still, in alcohol, if practicable, and one half of the solution mixed with tartaric acid, the other half with bichloride of platinum.   Should potassa be present, the tartaric acid will, after the lapse of some time, produce a colorless, granular, crystalline precipitate, and the bichloride of platinum will produce a yellow precipitate. (Vide § 86. *a.*)

2. MAGNESIA IS PRESENT.   The ignited residue of § 123. **161** 1. (157) is dissolved in water, baryta water added, as long as a precipitate continues to form. The fluid is then boiled with the precipitate, filtered from the latter, and an excess of a mixture of carbonate of ammonia with some caustic ammonia added to the filtrate.   A gentle heat is then applied, and continued for some time ; the solution is afterwards filtered, the filtrate evaporated to dryness, and the residue ignited, to remove the ammoniacal salts. The residue, after being heated to redness, is dissolved in a small quantity of water, and filtered if necessary (a little carbonate of baryta dissolved by the ammo-

niacal salts, in general, remaining) ; then proceed with the
residue according to § 124. 1. (160.)

<div align="center">§ 125.</div>

We come, finally, to the examination for ammonia. A **162**
portion of the substance, or fluid, under examination, is
treated with an excess of hydrate of lime, and if necessary a
little water. The ammoniacal odor of the evolved gas, its
property of restoring the blue color of reddened litmus paper,
and forming white fumes with hydrochloric acid, demonstrate
the presence of ammonia.

Compounds in which all the more frequently occurring acids **163**
and bases, metals and metalloids, are supposed to be
present.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF
THE ACIDS AND METALLOIDS.

<div align="center">I. *In the absence of Organic Acids.*</div>

<div align="center">§ 126.</div>

1. For the detection of ARSENIOUS and ARSENIC ACIDS,
CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID,
compare § 111. 1. (67) and (68) 2.

2. A portion of the solution is mixed with nitrate of baryta,
and neutralized with ammonia, should this be necessary.

   a. No PRECIPITATE IS FORMED. Absence of sulphuric
   acid, phosphoric acid, boracic acid, chromic acid, silicic
   acid, oxalic acid, arsenious and arsenic acids.* Pass
   over to 3.

   b. A PRECIPITATE IS FORMED. The fluid is diluted,

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* Should an ammoniacal salt be present in the fluid under examination,
the non-formation of a precipitate cannot be considered a conclusive proof of
the absence of oxalic acid, arsenious and arsenic acids, and more particu-
larly of boracic acid, since the baryta salts of these acids are not insoluble
in water, in presence of ammoniacal salts.

and hydrochloric acid added ; if the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present.

3. Nitrate of silver is added to a portion of the solution, **165** which if acid is previously to be EXACTLY neutralized, by means of ammonia, and if alkaline, by means of nitric acid. *

a. No PRECIPITATE IS FORMED. Pass over to 4 (**169**) ; neither chlorine, iodine, cyanogen, phosphoric acid, silicic acid, oxalic acid, nor chromic acid are present ; nor boracic acid, if the solution was not too dilute.

b. A PRECIPITATE IS FORMED. After noticing the **166** color of the precipitate, it is treated with nitric acid.

a. The precipitate redissolves completely. Pass over to 4 (**169**) ; for neither chlorine, iodine, nor cyanogen are present.

β. There is a residue : CHLORINE, IODINE, or CYANOGEN. The residue is washed, and then digested with ammonia.

aa. There is a yellowish residue. Iodine. The **167** reaction with starch (vide § 101. *c.*) is resorted to as a conclusive proof of the presence of this element. The solution is filtered from the undissolved residue, and nitric acid in excess added to the filtrate ; if a precipitate is formed, it indicates chlorine or cyanogen, and is to be further examined, as directed in *bb.*

bb. There is no residue; CHLORINE or CYANOGEN ; **168** absence of iodine. The ammoniacal solution is again precipitated with nitric acid. Before proceeding further in this examination, the analyst should ascertain whether cyanogen is present or not. For this purpose a portion of the original solution is warmed with solution of ferroso-ferric oxide of iron,

* This operation offers no difficulty and requires but little time for its performance, if the analyst has taken care to dilute the nitric acid or ammonia considerably.

and hydrochloric acid added. The formation of a blue precipitate indicates the presence of CYANO- GEN. * If no precipitate form, and the fluid does not acquire a blue tint, the precipitate redissolved by the ammonia consists only of chloride of silver, and there is no necessity for further examination. But if this preliminary examination has revealed the presence of cyanogen, the precipitate produced by nitric acid in the ammoniacal solution is to be further examined, to distinguish between the chlo- ride of silver, and cyanide of silver. The precipitate is accordingly washed, taken from the filter while still moist, dried in a porcelain crucible, and ignited; when the chloride of silver will simply fuse, whilst the cyanide will undergo reduction, attended with formation of some paracyanide of silver. The pre- sence of chlorine may now be readily demonstrated, by placing a fragment of zinc upon the residual mass, pouring water over it which contains some sulphuric acid in admixture, waiting until the evo- lution of hydrogen ceases, filtering, diluting the filtrate with water, and adding solution of nitrate of silver.

4. The aqueous solution is tested for NITRIC ACID, by **169** mixing with solution of indigo until the fluid acquires a light blue tint, adding some sulphuric acid, and applying heat; also by treating the solution with one third its amount of con- centrated sulphuric acid, and throwing a crystal of protosul- phate of iron into the mixture. The presence of nitric acid is demonstrated, in the first case, by the decoloration of the blue solution, and, in the second case, by the formation of a layer of brown fluid around the crystal. (§ 102. a.)

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* Should the cyanogen be present as free hydrocyanic acid, which may be readily recognized by its characteristic odor, this acid is to be saturated with potassa before adding the solution of ferroso-ferric oxide. That nitrate of silver fails to detect the cyanogen in some compounds, (in cyanide of mercury, for instance,) has been mentioned already at § 101 d.

I have now still to speak of the examinations for phos-
phoric acid, boracic acid, silicic acid, oxalic acid, and chro-
mic acid.   Testing for these acids is necessary only in cases
where both chloride of barium, and nitrate of silver have pro-
duced precipitates in neutral solutions.   Compare note to
§ 126. 2. *a.* (164).

5. If the precipitate produced by nitrate of silver be of a **170**
yellowish color, the analyst has to look more particularly for
the presence of phosphoric acid.   To detect this acid, am-
monia in excess, with chloride of ammonium, and afterwards
sulphate of magnesia, are added to a portion of the fluid which
must then be well shaken or stirred.   The formation of a
crystalline precipitate demonstrates the presence of PHOSPHO-
RIC ACID.   The reaction with perchloride of iron and acetate
of potassa, which I have described at § 99. *a.* 8, may also be
had recourse to.

6. A small portion of the substance under examination is **171**
drenched with alcohol, sulphuric acid added, and the mix-
ture heated to boiling in a small crucible : the alcohol is
then kindled.   If the flame presents a green tint, BORACIC
ACID is present.   Should copper be present, this must first
be removed either by means of sulphuretted hydrogen, or by
boiling the fluid with an excess of potassa. *

7. If the fluid become red, or yellow changing to red, upon **172**
the addition of hydrochloric acid, and if the precipitate pro-
duced by nitrate of silver in the neutral solution has a purple
red color, the presence of CHROMIC ACID is confirmed.

8. For SILICIC ACID test as § 100. *b.* 2. directs.

9. To effect the detection of OXALIC ACID, solution of sul-
phate of lime is added to a portion of the fluid under exami-
nation, which, should it manifest acid reaction, is to be
neutralized with ammonia.   The formation of a white
precipitate, insoluble in acetic acid, demonstrates the presence
of oxalic acid.

* Should the substance which it is intended to treat for boracic acid be a
fluid, this must first be evaporated to dryness, and the residue operated upon
with alcohol and sulphuric acid, in the manner described.

CHLORATES, BROMIDES, and FLUORIDES, are of less frequent **173**
occurrence.   The presence of chlorates is already indicated
by the violent deflagration which ensues upon fusing the salt
under examination, with charcoal.   (Vide § 107. A. I. 2. *c.*)
(6).   To demonstrate the presence of chloric acid, a sample
of the solid salt is heated in a test-tube, and a smouldering
wood splinter introduced into the tube ; when the presence of
CHLORIC ACID will be confirmed by the kindling of the
splinter.   Nitrate of silver will, in that case, produce a
copious precipitate of chloride of silver, in the aqueous solu-
tion of the residue.   The reaction with concentrated sulphuric
acid, (§ 102. *b.* 8) or fusion with cyanide of potassium,
(§ 102. *b.* 4.) may likewise be resorted to.   The detection of
BROMIDES is simple, if iodides are not at the same time pre-
sent.   I refer to § 101 for the manner of effecting the
positive detection of bromine in either case.   With regard to
the detection of FLUORIDES, the methods described § 99, *d.* 4
and 6, are the most efficient under all circumstances.

Compounds in which all the more frequently occurring acids
   and bases, metals and metalloids, are supposed to be
   present.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF **174**
THE ACIDS AND METALLOIDS.

II. *In presence of organic acids.*

§ 127.

I. CHROMIC ACID, ARSENIOUS and ARSENIC ACIDS, have
already been detected in the course of testing for the bases ;
concerning the distinction of arsenious from arsenic acid,
compare § 95. additions and remarks.
  2. Hydrochloric acid is added to a portion of the solution. **175**
The formation of a precipitate, which, when heated on a
platinum plate, volatilizes partly, or totally, emitting the

characteristic odor of BENZOIC ACID, indicates the presence
of this acid.   Effervescence, upon the addition of hydro-
chloric acid, may be caused by the presence of CARBONIC ACID,
or SULPHURETTED HYDROGEN.   (Vide § 111. 2. (68).

3. Ammonia is added to a portion of the solution, until the **176**
latter acquires a feebly alkaline reaction; it is then filtered
if necessary, chloride of barium added, and the mixture
heated to boiling.

Should hydrochloric acid have produced a precipitate
in the original solution, the filtrate of this is to be used
for the present experiment.

a. No PRECIPITATE IS FORMED.   Absence of sul-
phuric acid, phosphoric acid, chromic acid, silicic acid,
boracic acid, arsenic acid, arsenious acid, oxalic acid,
tartaric acid, citric acid; these acids may, therefore, be
disregarded in the subsequent course of examination.
The remarks made in the note to § 126. 2. *a.* **(164)**
apply equally to the last six of these acids.

b. A PRECIPITATE IS FORMED.   Dilute hydrochloric **177**
acid is added.

a. The precipitate redissolves : Absence of sul-
phuric acid.

β. There is a residue : SULPHURIC ACID.

4. Nitrate of silver is added to a portion of the solution, **178**
which must first be EXACTLY neutralized with nitric acid, if
alkaline, and with ammonia, if acid.   (Compare note to
§ 126. 3. **(165)**.

a. No PRECIPITATE IS FORMED : absence of phos-
phoric acid, boracic acid, chromic acid, silicic acid,
oxalic acid, tartaric acid, citric acid; these may there-
fore be disregarded in the further course of examination.

b. A PRECIPITATE IS FORMED.

a. It is white or yellow. A portion of the fluid, **179**
with the precipitate suspended in it, is boiled. Speedy
and complete reduction indicates FORMIC ACID.   The
reaction with protonitrate of mercury may be had
recourse to as a conclusive test, (§ 105. *b.*)   I have to

refer, however, in this respect, to the remark which
will be found at the end of this number, (4.)   The
rest of the precipitate is treated with nitric acid.   If
it dissolves, neither CHLORINE, IODINE, nor CYANOGEN,
are present; but if the nitric acid fails to effect its
complete solution, the residue is to be tested for these
salt radicals according to the directions of § 126. 3.
b. β. (166).

β. The precipitate produced by nitrate of silver is **180**
purple red : CHROMIC ACID.   Should arsenic acid be
present, acetate of lead must be added to a fresh
sample of the solution : when the formation of a yellow
precipitate proves the presence of chromic acid.
CHLORINE, IODINE, and CYANOGEN, may likewise be
present in the silver precipitate : test for these salt
radicals as § 126. 3. b. β. (166) directs.

Should both chromic, and formic acids be present
the reduction of oxide of silver, and of protoxide of
mercury is not a positive proof of the presence of
formic acid ; this can be obtained only by the follow-
ing method :—The original solution is decomposed
with nitric acid, then agitated with excess of oxide of
lead and filtered ; the filtrate, after the addition of sul-
phuric acid in excess, is distilled.   Test the distillate
according to § 105. b.

5. Should chloride of barium and nitrate of silver have **181**
produced precipitates, the analyst has to test for PHOSPHORIC
ACID, according to the direction of § 126. 5 (**170**), and for
SILICIC ACID as directed at § 100. b. 2.

6. Should the solution have an acid reaction, a portion of **182**
it is neutralized with potassa, evaporated to dryness, and the
residue (or a portion of the original dry substance) introduced
into a small tube, some alcohol is then poured over it, and
concentrated sulphuric acid added, to the extent of about
one-third of the volume of the alcohol ; the mixture is now
heated to boiling.   Emission of the odour of acetic ether de-
monstrates the presence of ACETIC ACID.   This odor becomes

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in many instances more distinctly perceptible on agitating the cooling, or cool mixture. The contents of the tube are poured into a small crucible, heated, and kindled. A green flame denotes the presence of BORACIC ACID.

7. A portion of the fluid is made feebly alkaline by addi- **183** tion of ammonia, it is then filtered, if necessary, and chloride of calcium added. The mixture is vigorously shaken, and allowed to stand at rest from ten to twenty minutes. If the solution was neutral, the addition of the chloride of calcium is to be preceded by that of some chloride of ammonium.

   a. NO PRECIPITATE IS FORMED, EVEN AFTER THE LAPSE OF SOME TIME. Absence of oxalic acid and tartaric acid ; pass over to 8.

   b. A PRECIPITATE IS FORMED IMMEDIATELY, OR AFTER SOME TIME. The solution is filtered from the precipitate, and the filtrate tested as directed at 8.

   The precipitate is washed and digested, with an excess of cold slightly diluted solution of potassa, the operation being aided by agitation of the mixture. The solution is filtered and the filtrate boiled for some time ; should this cause the separation of a precipitate, TARTARIC ACID is present.

   Solution of sulphate of lime is added to a portion of the original solution which, if acid, is first to be neutralized with ammonia. The formation of a precipitate, which does not disappear upon the addition of acetic acid, but is re-dissolved by hydrochloric acid, demonstrates the presence of OXALIC ACID.

8. The fluid in which chloride of calcium has failed to pro- **184** duce a precipitate, or that which has been filtered from the precipitate—(in which latter case some more chloride of calcium is to be added)—is mixed with alcohol.

   a. NO PRECIPITATE IS FORMED. Absence of citric acid and of malic acid. Pass over to 9.

   b. A PRECIPITATE IS FORMED. The solution is filtered and the filtrate treated as directed at 9. The

precipitate is washed with alcohol, and dissolved on the filter in the least possible amount of dilute hydrochloric acid; the solution is mixed with ammonia to feebly alkaline reaction, and boiled for some time.

a. THE FILTRATE REMAINS CLEAR. Absence of **185** citric acid. Presence of MALIC ACID ; alcohol is again added to the fluid, and the lime precipitate which forms is ignited, when the actual presence of malic acid will be demonstrated by the conversion of the precipitate into carbonate of lime, attended with separation of charcoal ; the reaction with acetate of lead is resorted to as a confirmatory proof. § 103. e. 5.

β. A HEAVY, WHITE PRECIPITATE IS FORMED. Presence of CITRIC ACID. The solution is filtered whilst boiling, and the filtrate tested for malic acid, in the same manner as at a.

9. The filtrate of 8 b. (or the fluid in which addition of **186** alcohol has failed to produce a precipitate, § 127. 8. a. (**184**) is heated to expel the alcohol, and exactly neutralized with hydrochloric acid ; perchloride of iron is then added to the neutralized fluid. Should this fail to produce a light brown flocculent precipitate, neither succinic nor benzoic acid are present. Should a precipitate of this kind be formed, it proves the presence of SUCCINIC ACID, unless benzoic acid has been previously detected. Should this have been the case, the solution is to be fitered from the precipitate, the latter washed and digested with ammonia in excess ; the mixture is then to be filtered, the filtrate slightly evaporated, and tested for SUCCINIC ACID with chloride of barium and alcohol. (Compare § 104. additions and remarks.)

10. Test for NITRIC ACID according to the directions of § 126. 4. (**169**).

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE **187** IN HYDROCHLORIC ACID, AND IN NITRIC ACID. DETECTION OF THE ACIDS, AND METALLOIDS.

1; *Absence of Organic Acids.*

§ 128.

In the examination of these compounds the analyst has to look for all the acids occurring at § 126, with the single exception of chloric acid. Cyanogen compounds are not examined after this method : compare § 131.

1. The remarks made at § 114. 2. (**90**) upon ARSENIOUS and ARSENIC ACIDS, HYDROSULPHURIC ACID, CARBONIC ACID, and CHROMIC ACID, are equally applicable here.

2. A portion of the substance is boiled with nitric acid, **188** and the solution filtered, if necessary.

    a. Effervescence takes place; this may be caused by CARBONIC ACID, or NITRIC OXIDE GAS ; the presence of the former may be demonstrated according to the directions of § 100. *a.* 3.; the latter usually indicates the presence of a sulphur compound.

    b. Violet fumes escape,. which impart a blue tint to starch : IODINE.

3. Nitrate of silver is added to a portion of the nitric acid **189** solution.

    a. No PRECIPITATE IS FORMED : absence of chlorine; pass over to 4.

    b. A PRECIPITATE IS FORMED. The solution is filtered off, the precipitate washed, and digested with ammonia; if it redissolves totally, or partly, CHLORINE is present.

4. Some of the substance under examination is boiled with hydrochloric acid, and the solution filtered, if necessary. A portion of the solution, or filtrate diluted with water is mixed with chloride of barium. The formation of a precipitate indicates SULPHURIC ACID.

5. Another portion of the hydrochloric acid solution is **190** tested for NITRIC ACID, with indigo, and protosulphate of iron. (Vide § 126. 4. (**169**). In many instances, the presence of the nitric acid will have been revealed at an early stage of the examination, by the deflagration which ensues upon exposing nitrates, on a charcoal support, to the blow-pipe flame.

6. Should the test of § 128. 2. *b.* (**188**) have given no **191** evidence of the presence of iodine, a portion of the substance under examination is to be heated with concentrated sulphuric acid. If any IODINE compound be present, violet vapors will be evolved, which impart a blue tint to starch. (Compare § 101. *c.* 7.)

7. Test for BORACIC ACID by treating a sample of the substance with sulphuric acid, and alcohol. (Vide § 99. *b.* 5.)

8. The fluid of § 124, from which the metals have been re- **192** moved, and which has been reserved for this stage of the examination, according to the directions of that paragraph, is now tested for PHOSPHORIC ACID, according to § 126. 5. (**175.**) Should this acid have been combined with baryta, strontia, lime, magnesia, or alumina, its presence will already have been discovered in the course of examination for the bases. Any oxalic acid that may be present in the same liquid, can be detected according to the method given in § 126. 9. (**172.**), if it is not combined with lime, baryta, or strontia; should the latter be the case, § 129. 2. (**194.**) must be followed.

9. Test for SILICIC ACID as directed at § 100. *b.* 3. With regard to the more rarely occurring BROMINE and FLUORINE compounds, I refer to the remarks made at the end of § 126.

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, AND IN NITRIC ACID. DETECTION OF THE ACIDS, AND METALLOIDS.

II. *In presence of Organic Acids.*

§ 129.

1. Test for CARBONIC ACID, ARSENIC ACID, ARSENIOUS ACID, **193** SULPHURIC ACID, NITRIC ACID, BORACIC ADID, CHROMIC ACID, SILICIC ACID, CHLORINE, IODINE, and SULPHUR, as directed at § 128 ; and for ACETIC ACID as directed at § 127. 6. **(182.)** CYANOGEN compounds are not examined after this method : compare § 131.

2. A portion of the compound under examination is dis- **194** solved in hydrochloric acid, and the solution filtered from the undissolved residue that may remain, and which is afterwards to be tested for BENZOIC ACID, as directed at § 127. 2. **(175.)** The filtrate is mixed with an excess of solution of carbonate of potassa, and the mixture boiled for some time. The fluid is filtered from the precipitate formed, and the filtrate saturated with dilute hydrochloric acid, is tested for PHOSPHORIC ACID and OXALIC ACID, as directed at § 126. 5. **(170.)** and 9. **(172.)** ; and for TARTARIC ACID, CITRIC ACID, MALIC ACID, SUCCINIC ACID, and BENZOIC ACID, strictly according to the directions of § 127. 7. 8. and 9. **(183—186.)** As regards phosphoric acid, this method is not to be entirely depended on ; it is therefore better, to test the hydrochloric acid solution of the original substance with molybdate of ammonia, according to § 121. 1. *a.* **(138.)**

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

B. SUBSTANCES INSOLUBLE, OR SPARINGLY SOLUBLE, BOTH IN WATER, AND IN HYDROCHLORIC ACID. DETECTION OF THE BASES, ACIDS, AND METALLOIDS.

§ 130.

The following substances and compounds belong to this **195** class :—

SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, CHLORIDE OF SILVER, CHLORIDE OF LEAD, SUL-PHATE OF LEAD, SULPHURET OF MERCURY, BISULPHURET OF MERCURY, PROTOCHLORIDE OF MERCURY, SEVERAL OF THE FERRO and FERRICYANIDES, SEVERAL SULPHURETS, SILICIC ACID, SULPHUR and CARBON.

Besides the above, a few acid arseniates belong to this class ; they are, however, of rare occurrence in the ana-lysis of the more important—(in a pharmaceutical and technical point of view)—mixtures and compounds, as the insoluble modification of the oxide of chromium, the ignited peroxide of tin, and the fluoride of calcium. Of these latter less frequently occurring substances, I purpose to treat sepa-rately.

With regard to the insoluble cyanides, I refer to § 131.

A. THE RESIDUE IS WHITE. It may in that case contain **196** of the substances above enumerated, SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, SULPHATE OF LEAD, CHLORIDE OF LEAD, CHLORIDE OF SILVER, PROTO-CHLORIDE OF MERCURY, SILICIC ACID, SULPHUR.

No attention need be paid to the presence of sulphate of lime, unless this substance has been already detected in the aqueous solution. The lead compounds also may be disre-garded, if the previous examination has not revealed their presence.

1. A sample of the substance under examination is heated **197**

on a platinum plate, and the flame made to play upon it. Emission of the odor of sulphurous acid demonstrates the presence of SULPHUR. If there is no residue, sulphur alone is present. If, however, the heat applied was very intense, protochloride of mercury may also have volatilized. The outward appearance of the residue will suffice to show whether this is to be apprehended.

2. Hydrosulphuret of ammonia is added to a very small **198** portion of the substance under examination.

    a. It remains white. Absence of metal compounds. Pass over to 3. (**203**.)

    b. It turns black. This is a positive proof of the presence of a metallic salt, which may be either protochloride of mercury, chloride of silver, chloride of lead, or sulphate of lead. Moreover, all the other compounds enumerated under A. may be present. The further process varies according to the presence or absence of lead.

The following preliminary test is applied to ascertain which method ought to be pursued:

A small portion of the substance is mixed with carbonate of soda, and the mixture exposed to the reducing flame of the blow-pipe. The production of a metallic grain, (which is oxidized in the outer flame,) attended with yellow incrustation of the charcoal, indicates lead.

    a. THIS PRELIMINARY EXAMINATION INDICATES **199** THE PRESENCE OF LEAD IN THE WHITE RESIDUE.

      aa. The greater portion of the residue (which, if moist, must first be dried) is fused with three parts of dry carbonate of soda and three parts of cyanide of potassium, in a small porcelain crucible, over a spirit-lamp. The mass fuses readily; it is maintained in this state for some time. After cooling, the mass is boiled with water, the fluid filtered from the residue, and the latter very carefully washed. The greater portion of the filtrate is supersaturated with hydrochloric acid, and a small quantity of this

acidified solution tested with chloride of barium.
The formation of a precipitate indicates the pre-
sence of a SULPHATE. (Should a precipitate (silicic
acid) be formed, upon supersaturating the filtrate
with hydrochloric acid, the fluid is to be diluted,
and filtered from the precipitate formed, the filtrate
being then tested for sulphuric acid.) The rest of
the acidified portion of the filtrate is evaporated to
dryness, and treated with water. Should there be
a residue, this consists of SILICIC ACID. The for-
mation of a clear glass, upon fusing the residue
with carbonate of soda in the blow-pipe flame, is a
conclusive proof of the presence of this substance.
The rest of the filtrate, which has not been mixed
with hydrochloric acid, is acidified with nitric acid,
and boiled until it ceases to emit the slightest odor
of hydrocyanic acid; nitrate of silver is then added;
the formation of a precipitate of chloride of silver
denotes that the residue, insoluble in water and
hydrochloric acid, contains a CHLORIDE, (provided
always, the reagents used be pure, and the residue
entirely free from soluble chlorine compounds.
The insoluble portion that remained upon treating
the fused mass with water, and which has been
thoroughly washed, is now treated with acetic acid;
if it dissolves partly in this acid with effervescence,
there is a positive proof of the presence of sul-
phates of the alkaline earths. If no effervescence
takes place, the absence of the sulphates of the
alkaline earths is proved. If effervescence has
taken place, a portion of the acetic acid solution is
tested with sulphuretted hydrogen. If a black pre-
cipitate (sulphuret of lead) forms, the lead is re-
moved in the same manner from the whole of the
acetic acid solution, and the filtrate—(which, if
necessary, is first to be concentrated by evapora-
tion—treated as § 122. directs, beginning at 2. *a.*

(153). Should the sample of the acetic acid solu-
tion remain unaltered when tested with the sul-
phuretted hydrogen, the remainder is treated at
once according to the directions of § 122. 2. *a*.
(153). The residue, insoluble in acetic acid, is
treated with nitric acid, and a small portion of the
solution, from which the excess of acid has been
removed by evaporation, is tested with sulphuric
acid for lead. The rest of the solution is consider-
ably diluted with water, and tested for SILVER, with
hydrochloric acid. If nitric acid leaves a residue,
this consists of undecomposed silicic acid, or of an
incompletely decomposed sulphate of one of the
alkaline earths.

bb. Half of the remainder of the residue is boiled **200**
with carbonate of potassa. Should this change the
white color of the residue to grey or black, PROTO-
CHLORIDE OF MERCURY is present. To obtain posi-
tive conviction on this point, the other half is to be
heated with dry carbonate of soda in a small glass
tube. (Vide § 91. *b*. 8.)

β. THE PRELIMINARY EXAMINATION PROVES THAT **201**
THE WHITE RESIDUE CONTAINS NO LEAD. The whole
of the residue is drenched, and digested for some time,
with hydrosulphuret of ammonia in excess, the fluid
is filtered from the precipitate formed, and the latter
washed and subsequently boiled with nitric acid.

*aa. The precipitate dissolves, with the exception
of the separated sulphur*. CHLORIDE OF SILVER
alone is present. In confirmation, the nitric acid
solution is tested for silver, with hydrochloric
acid. To demonstrate the presence of the chlo-
rine, the fluid filtered from the sulphuret of silver
formed, is supersaturated with nitric acid, boiled in
order to expel the sulphuretted hydrogen, and fil-
tered from the sulphur which has separated ; the
filtrate is then tested with nitrate of silver.

bb. There is a residue, besides the separated **202** *sulphur.*

αα. THIS RESIDUE IS BLACK : MERCURY. The fluid is filtered from the residue, and the filtrate tested for silver, with hydrochloric acid ; the residue is heated with aqua regia. Should this effect complete solution, with the exception of the separated sulphur, the investigation may be considered at an end, the absence of the sulphates of the alkaline earths and that of silicic acid being fully proved ;—should there be a white residue, this is to be washed, and treated as directed at § 130. A. 3. (**203**.) The solution in aqua regia is tested with a clean piece of copper, or with protochloride of tin to obtain positive proof of the presence of mercury, (vide § 120. 2.) (**134**.)

To demonstrate the presence of the chlorine, the hydrosulphuret of ammonia fluid filtered from the mixed precipitate is treated as directed at αα.

ββ. THE RESIDUE IS NOT BLACK : absence of mercury. For the further process, vide 3.

3. This residue (ββ) or the original residue of § 130. A. 2. **203** *a.* (**198**) is fused in a platinum crucible, * over a Berzelius spirit-lamp or gas, with four parts of carbonate of potassa and soda ; the fused mass is treated with water, boiled, filtered, and the residue which may remain washed until chloride of barium ceases to produce a precipitate in the washing water. (This water must not be added to the filtrate.) The residue is treated as directed at 4. The filtrate is supersaturated with hydrochloric acid, and a portion of it tested with chloride of barium ; the formation of a precipitate indicates the pre-

* A porcelain crucible may be substituted for a platinum crucible, in which case, six parts of a mixture of equal parts of dry carbonate of soda, and cyanide of potassium must be employed, instead of the carbonate of potassa, and soda ; the method in the text is however the best.

sence of SULPHATES OF THE ALKALINE EARTHS. The rest of the filtrate is evaporated to dryness and the residue treated with water; should anything remain undissolved, this consists of SILICIC ACID.

4. The residue remaining upon boiling the fused mass with **204** water, (vide 3.) denotes the presence of SULPHATES OF THE ALKALINE EARTHS. It is carefully washed and treated with hydrochloric acid. Should the residue dissolve totally, or partly, being attended in either case with effervescence, this is a positive proof of the presence of sulphates of the alkaline earths. The hydrochloric acid solution is then tested according to the directions of § 122, beginning at 2. *a*. (**153**.) Should the hydrochloric acid leave a residue, this consists of silicic acid, or of an imperfectly decomposed sulphate of one of the alkaline earths.

B. THE RESIDUE IS NOT WHITE. The presence of some **205** substances (cinnabar, sulphuret of arsenic) may sometimes be inferred, from the mere color of the residue.

1. Test for SULPHUR, according to the directions of § 130. A. 1. (**197**.)

2. The greater portion of the residue is treated with aqua regia and the mixture boiled ; the solution is filtered whilst still hot, and, should there be a residue besides the separated sulphur, this is once more boiled with water, the fluid filtered, and this second filtrate added to the first. The whole of the filtrate is then evaporated nearly to dryness, and the residual mass redissolved in water ; one portion of the solution is tested for LEAD, with sulphuric acid, and another portion for MERCURY, with a clean piece of copper. If hydrochloric acid has been used as a solvent in the examination for the bases (§ 109.), the solution in aqua regia must be tested for the metals in the usual way, since various other sulphurets, insoluble, or sparingly soluble in hydrochloric acid, might be present.

3. If aqua regia has left a residue, besides the sulphur **206** which may have separated, it is to be thoroughly washed. Should a compound of lead have been present, hot water is

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to be used for washing, and the process continued until hydrosulphuret of ammonia ceases to blacken the fluid which runs off.

    a. THE RESIDUE IS WHITE : a portion of it is **207** tested with hydrosulphuret of ammonia.

        a. It becomes black. The whole of the residue is digested with hydrosulphuret of ammonia, and the further process conducted according to the directions of § 130. A. 2. *b. β.* (**201.**)

        β. It remains white. The residue is treated as directed at § 130. A. 3. (**203.**)

    b. THE RESIDUE IS BLACK; this indicates the pre- **208** sence of carbon in some form : charcoal, coal, bone-black, graphite, &c. A portion of the residue is ignited in a small platinum spoon, or in the blow-pipe flame. If entirely consumed this is a proof of the exclusive presence of carbon, but if there is a residue, or if the combustion is not complete (graphite), the analyst has also to look for CHLORIDE OF SILVER, SULPHATES OF THE ALKALINE EARTHS, and SILICIC ACID ; the residue in that case is treated as directed at § 130. B. 3. *a. a.* (**207.**)

4. Of the acids, and electro-negative substances, besides **209** those already mentioned, only CHLORINE, and SULPHURIC ACID can be present. To detect chlorine, and sulphuric acid, part of the insoluble residue from the first solution in hydrochloric acid is digested with hydrosulphuret of ammonia, the fluid divided into two parts, the one half boiled with hydrochloric acid in excess, and the other half with nitric acid in excess; both solutions are filtered, the former is tested with chloride of barium for sulphuric acid, the latter with nitrate of silver for chlorine.

The insoluble PEROXIDE OF TIN and OXIDE OF CHROMIUM **210** may be detected before the blow-pipe. Peroxide of tin, when exposed on charcoal, with carbonate of soda and cyanide of potassium, to the reducing flame of the blow-pipe, yields a soft metallic grain, without incrustation of the charcoal. Oxide

of chromium, distinguished also by its green color, is treated with phosphate of soda and ammonia, as directed at § 88. *b.* 6., or fused with carbonate of soda and nitrate of potassa (§ 88. *b.* 5). The arsenic acid of the insoluble ARSENIATES is detected before the blow-pipe, and by reduction in a glass tube. (Vide § 95. *e.* 7). To effect the detection of the bases these insoluble arseniates must first be decomposed by boiling with concentrated sulphuric acid. FLUORIDE OF CALCIUM is decomposed by concentrated sulphuric acid, in a platinum crucible: the fluorine is detected by its property of etching glass; the lime remains as sulphate of lime. There are still several other compounds which, after ignition, become insoluble in acids, but it would exceed the limits of this work to treat of them all.

§ 131.

SPECIAL METHOD FOR THE DECOMPOSITION OF CYANIDES, 211 FERROCYANIDES, &c.* WHICH ARE INSOLUBLE IN WATER.

The analysis of compounds of this description by the general method, frequently gives rise to the manifestation of fallacious phenomena which tend to mislead the analyst. Acids, moreover, often fail to effect the complete solution of these compounds. For these reasons it is advisable to analyze them by the following special method: The substance is thoroughly extracted with water; the residue boiled with strong solution of potassa, and, after the mixture has been in ebullition a few minutes, some solution of carbonate of potassa is added, and the whole mixture again boiled.

 a. COMPLETE SOLUTION ENSUES. Absence of alka- 212 line earths, nickel, cadmium, bismuth, and silver. Sulphuretted hydrogen water is added in excess to the alkaline solution:

  a. No permanent precipitate is formed. Absence of zinc, lead, copper.† Nitric acid is added to the

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 * The student is advised to read the additional remarks to § 131. (vide section II.) before entering upon this course of analysis.

 † I have included oxide of copper among the number of oxides which are

alkaline fluid to acid reaction, and should the mixture
not yet smell strongly of sulphuretted hydrogen, also
an excess of solution of the latter reagent.

    aa. No precipitate is formed. Absence of mer- **213**
cury, tin, arsenic, antimony, gold, and platinum.
The solution can contain only alumina, and those
metals which form compound radicals with cyano-
gen. A sample of the fluid is tested for CYANOGEN,
by successive addition of potassa, solution of ferroso-
ferric oxide, and hydrochloric acid. The remain-
der of the fluid is evaporated to dryness and the
residue heated to fusion. The fused mass is poured
out upon a broken piece of porcelain, and after-
wards boiled with water; the solution is then fil-
tered from the residue, which is subsequently tested
for IRON, MANGANESE, COBALT, and ALUMINA. The
filtrate is tested for CHROMIC ACID (in which form
the analyst will obtain the whole of the chromium
present) with acetate of lead, after previous addi-
tion of acetate of potassa; and for the other acids
which may be present, according to the directions
of § 126.

    bb. A precipitate forms. The fluid is filtered **214**
from the precipitate, which is then examined for
mercury, and the metals of the sixth group, accord-
ing to the directions of § 118. 3. (**116.**) The filtrate
is tested for cyanogen, alumina, iron, manganese,
cobalt, chromium, and the acids, as directed at *aa.*
(**213.**)

    β. A precipitate is formed. The fluid is filtered off **215**
from the precipitate, which is then dissolved in nitric
acid, and the solution treated according to the direc-
tions of § 117. III. (**109**), bearing in mind that ZINC,

soluble in potassa, because the hydrated oxide of copper remains suspended
in concentrated solution of potassa in a state of extreme division, and does
not separate even upon boiling : the blue fluid which is thus produced looks
so like a real solution that it can scarcely be distinguished from one.

LEAD, COPPER (and MERCURY) alone can be present. The filtrate is treated according to the directions of § 131. *a. a.* **(212.)**

b. THERE IS A RESIDUE. Water is added to the **216** alkaline fluid; the mixture is then boiled once more, and filtered. The residue is dissolved and examined according the directions of § 109. A. 2. **(35.)** The filtrate is treated as directed at § 131. *a.* **(212.)**

§ 132.

GENERAL RULES FOR THE DETECTION OF INORGANIC SUB- **217** STANCES IN CASES WHERE ORGANIC SUBSTANCES ARE PRESENT, WHICH BY THEIR COLOR, CONSISTENCE, OR OTHER PROPERTIES, IMPEDE THE APPLICATION OF THE REAGENTS, OR OBSCURE THE PHENOMENA PRODUCED.

Cases of this kind, as I have stated already in my introductory remarks to Part II., are so manifold, that it is impossible to lay down a method for every individual case; I will therefore confine myself here to the description of a few methods, such as are most generally applicable, and leave the adaptation of the modifications which individual cases may require, to the judgment of the analyst.

1. THE SUBSTANCE DISSOLVES IN WATER, BUT THE SOLU- **218** TION IS DARK COLORED, OR OF A SLIMY CONSISTENCE.

a. A portion of the solution is boiled with hydrochloric acid, and chlorate of potassa gradually added until the mixture is decolorized, and perfectly fluid; the solution is then heated until it ceases to emit the odor of chlorine; it is now diluted with water, and filtered. The filtrate is examined in the usual way, beginning at § 118. **(110.)**

b. Another portion of the solution is boiled for some **219** time with nitric acid, filtered, and the filtrate tested for silver, potassa, and hydrochloric acid. This method is frequently preferable to all others in cases where the

nitric acid succeeds in effecting the ready, and complete destruction of the coloring, and slimy matters, &c.

c. ALUMINA and OXIDE OF CHROMIUM might escape detection by this method, because ammonia and hydro-sulphuret of ammonia fail to precipitate these oxides from fluids containing non-volatile organic substances in admixture. Should the analyst have reason, therefore, to suspect the presence of these oxides, he must defla-grate a third portion of the substance with nitrate of potassa, and some carbonate of soda, and boil the fused mass with water, when the chromium will be obtained in the solution in the form of chromic acid, whilst the alu-mina will be found in the residue.

2. BOILING WATER FAILS TO DISSOLVE THE SUBSTANCE, **220** OR EFFECTS ONLY PARTIAL SOLUTION.

The solution is filtered, and the filtrate treated either as di-rected at § 117, or, should it require decoloration, according to the directions of § 132. 1. **(218.)** Should the solution not admit of filtration, the further operation must be conducted as directed § 132. 2. c. **(221.)** The residue may be various :

a. IT IS FATTY. The fatty matters are removed by means of ether, and should there be a residue, this is treated as directed at § 109.

b. IT IS RESINOUS. Alcohol is used instead of ether, or both liquids are applied successively.

c. IT IS NEITHER OF THE ABOVE, e. g. woody fibre, **221** &c. The residue is dried, and the greater portion of it triturated with from three to four parts of pure nitrate of potassa; and the mixture gradually deflagrated in a red-hot crucible. The residue is treated as § 109. A. **(33)** directs. A portion of the original residue is boiled with aqua regia, the solution filtered, and the filtrate tested for mercury. The other part of the original residue is tested for ammonia, according to the directions of § 125.

§ 133.

IV.　CONFIRMATORY EXPERIMENTS.

When the various bases, acids, and electro-negative bodies, **222** present in the substance under examination have been detected, it is in many cases *advisable*, and in others even absolutely *necessary*, to control the results obtained. Many substances are so distinctly characterized by certain reactions, that their positive detection can readily be effected, even though the compound, or mixture under examination, may contain a great many other substances. For this purpose it is simply necessary to obtain these characteristic reactions in some fresh samples of the analysed body. But there are, on the other hand, a great many substances deficient in characteristic reactions. In this case the analyst should invariably endeavour to ascertain, by the strictest examination into the attendant circumstances, whether the reactions and phenomena which lead him to assume the presence of a certain substance may not be owing to extraneous causes. How often does it happen, for instance, that the presence of ammonia in a substance is deemed fully demonstrated, whilst in reality the reactions leading to this assumption, are simply owing to the presence of ammonia in the atmosphere of the laboratory ? How often is the presence of alumina unhesitatingly pronounced, simply because the solution of potassa used becomes turbid upon the addition of solution of chloride of ammonium, when the real cause of this turbidity is impurity of the potassa ? How frequently is iron or lime detected, because the filtering paper is not free from those bodies ?

As I have already, in the preceding part of the work, fully discussed the subject of reagents and reactions, I have only to observe that the selection of methods best adapted to control the results of any given analysis must be left to the discernment of the analyst.

CHAPTER II.

EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. ADDITIONAL REMARKS TO THE PRELIMINARY EXAMINATION.

To § § 106—108.

The inspection of the physical properties of a body may, as I have stated at § 106, in many cases enable the analyst to draw certain general (at least negative) inferences as to its nature. Thus, for instance, if the analyst is examining a white substance, he may at once conclude that it is not cinnabar, or if a light substance, that it is not a compound of lead, &c.

Inferences of this kind are quite admissible to a certain extent; but if carried too far they are apt to mislead the operator, by blinding him to every reaction not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, I may remark that small test-tubes, from two to three inches in length, may, in many cases, be substituted for iron spoons. They afford this advantage over the latter, that volatile bodies, organic substances, &c., are less likely to escape detection, and that a more correct and precise notion can be formed of the nature of the heated substance, than by exposure in an iron spoon. However, as every experiment would require a fresh tube, a spoon will be found more convenient and economical in experiments for practice.

With respect to the preliminary examination by means of the

blow-pipe, I have to remark that the student must avoid drawing positive conclusions from pyrochemical experiments, until he has acquired some practice in this branch of analytical chemistry. A slight incrustation of the charcoal support which may *seem* to denote the presence of a certain metal, is not always a *conclusive* proof of the presence of that metal, nor would it be safe to assume the absence of a substance simply because the blow-pipe flame has failed to effect reduction, &c., &c. The blow-pipe reactions are, indeed, in most cases unerring, but it is not always easy to produce them, and they are moreover liable to suffer modification by accidental circumstances.

The student should never omit the preliminary examination; the notion that this omission will save time, and trouble is very erroneous.

II. ADDITIONAL REMARKS TO THE SOLUTION OF SUBSTANCES, &c.

To § 109.

It is a task of some difficulty to fix the exact limit between substances which are soluble in water, and those that are insoluble in that menstruum, since the number of bodies which are sparingly soluble in water is very considerable, and the transition from *sparingly* soluble, to *insoluble* is very gradual. Sulphate of lime (which is soluble in four hundred and thirty parts of water) might perhaps serve as a limit between these two classes, since this salt may still be positively detected in aqueous solution, by the delicate reagents which we possess for lime and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon a platinum plate, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the nature of the substance; in this case the fluid is, in the first place, to be tested with litmus paper; a drop of solution of chloride of barium is then to be added to one portion of it, and some carbonate of potassa to another portion. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not examine it any further for bases or acids. If the fluid contained any of those bases or acids which principally form

sparingly soluble compounds, the chloride of barium, and carbonate of potassa would have revealed their presence. The analyst may therefore feel certain that the detection of the substance of which the residue left upon evaporation consists, will be more readily effected in the solution in hydrochloric or nitric acid, or aqua regia, as the case may be.

If water has dissolved any part of the substance under examination, the student will always do well to examine this solution for acids, and bases, since this will lead more readily to a correct apprehension of the nature of the compound—an advantage which will counterbalance the drawback of sometimes meeting with the same substance in the aqueous, and in the acid solution.

The following substances (with a few exceptions) are insoluble in water, but soluble in hydrochloric acid or in nitric acid: the phosphates, arseniates, arsenites, borates, carbonates, and oxalates of the earths and metals; and also several tartrates, citrates, malates, benzoates, and succinates, the oxides and sulphurets of the heavy metals, alumina, magnesia, many of the metallic iodides and cyanides, &c. Nearly the whole of these compounds are decomposed, if not by dilute, by boiling concentrated hydrochloric acid, (for the exceptions vide 130); but this decomposition gives rise to the formation of insoluble compounds when oxide of silver is present, and of sparingly soluble compounds in the presence of protoxide of mercury, and lead. This is not the case with nitric acid, and accordingly the latter effects complete solution in many cases where hydrochloric acid has left a residue. But, on the other hand, nitric acid leaves, besides those substances which are insoluble in simple acids, oxide of antimony, peroxide of tin, peroxide of lead, &c. undissolved, whilst it fails to effect the complete solution of many other substances. When, therefore, the compound under examination is not completely dissolved by nitric acid, (with the exception of the sulphur, which may separate in the case of sulphur compounds, or from silica,) the analyst is again referred to the hydrochloric solution, and thus exact limits are in some measure assigned to the third class of substances, viz. those which are insoluble in water and simple acids.

With regard to the solution of pure metals, or alloys, I have to

remark, that upon boiling them with nitric acid, white precipitates frequently form, although neither tin, nor antimony be present. Inexperienced students often confound such precipitates with the oxides of these two metals, although their external appearance is quite different   These precipitates consist simply of nitrates sparingly soluble in the nitric acid present, but readily soluble in water.   Consequently the analyst should ascertain whether these white precipitates will dissolve in water, or not, before he concludes them to consist of tin, or antimony.

III. ADDITIONAL REMARKS TO THE ACTUAL EXAMINATION.

To § 110—§ 132.

A. GENERAL SURVEY AND EXPLANATION OF THE ANALYTICAL COURSE.

a. DETECTION OP THE BASES.

The classification of the bases into groups, and the methods which serve to detect and isolate them individually, have been fully explained in Part I., Chapter III.   The systematic course of analysis from § 117 to § 125, is based upon this classification of the bases ; and as a correct apprehension of it is of primary importance, I will here subjoin a brief explanation of the grounds upon which this division rests.   Respecting the detection of the several bases individually, I refer the student to the additions and remarks to § 86—§ 95.   The general reagents which serve to divide the bases into principal groups are—HYDROCHLORIC ACID, SULPHURETTED HYDROGEN, HYDROSULPHURET OF AMMONIA, and CARBONATE OF AMMONIA ; this is likewise the order of succession in which they are applied.   Hydrosulphuret of ammonia performs a *double* part.

Let us suppose we have in solution the whole of the bases, together with arsenious acid, and phosphate of lime, (which latter may serve as a type for the salts of the alkaline earths, soluble

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in acids, and re-precipitated by ammonia from such solution
unaltered.

Chlorine forms insoluble compounds only with silver and
mercury; chloride of lead is sparingly soluble in water. The
insoluble protochloride of mercury corresponds with the protoxide
of mercury. If, therefore, we add to our solution;

1. *Hydrochloric acid.*

We remove from it the metallic oxides of the first section of the
fifth group, viz., the OXIDE OF SILVER and the PROTOXIDE OF
MERCURY. From concentrated solutions, a portion of the LEAD
may likewise precipitate as chloride; this is, however, immaterial,
as a sufficient quantity of the lead remains in the solution to per-
mit the subsequent detection of this metal.

Sulphuretted hydrogen completely precipitates the oxides of
the fifth and sixth group from solutions containing a free mineral
acid, since both the affinity of the metallic radicals of these oxides
for sulphur, and of hydrogen for oxygen, are sufficiently powerful
to overcome that between the metal and the oxygen, and between
the oxide and a strong acid, EVEN THOUGH THE ACID BE PRE-
SENT IN EXCESS. But none of the other bases are precipitated
under these circumstances, since those of the first, second, and
third group form no sulphur compounds insoluble in water; and
the affinity which the metallic radicals of the oxides of the fourth
group possess for sulphur, together with that manifested by hydro-
gen for oxygen, are not sufficiently powerful to overcome the
affinity either of the metal for oxygen or of the oxide for a strong
acid, IF THE LATTER IS PRESENT IN EXCESS.

. Accordingly, after the removal of the oxide of silver and pro-
toxide of mercury, by means of hydrochloric acid, if we add to our
solution, (which still contains free hydrochloric acid,)

2. *Sulphuretted hydrogen.*

We remove from it the rest of the oxides of the fifth, together
with those of the sixth group, viz., OXIDE OF LEAD, PEROXIDE OF

MERCURY, OXIDE OF COPPER, OXIDE OF BISMUTH, OXIDE OF
CADMIUM, PEROXIDE OF GOLD, PEROXIDE OF PLATINUM, PRO-
TOXIDE OF TIN, PEROXIDE OF TIN, OXIDE OF ANTIMONY, ARSE-
NIOUS ACID, and ARSENIC ACID. All the other oxides remain in
solution, either unaltered, or reduced to a lower degree of oxi-
dation, e. g. peroxide of iron, to protoxide ; chromic acid, to oxide
of chromium, &c.

The sulphurets corresponding to the oxides of the sixth group
combine with electro-positive metallic sulphurets (the sulphurets
of the alkaline metals) with which they form sulphur salts soluble
in water ; whilst the sulphurets corresponding to the oxides of the
fifth group do not possess this property. If, therefore, we treat
the whole of the sulphurets precipitated by sulphuretted hydrogen
from acid solution, with—

3. *Hydrosulphuret of ammonia,* or *sulphuret of potassium,*

the bisulphuret of mercury, and the sulphurets of lead, copper,
bismuth, and cadmium, will remain undissolved, whilst the other
sulphurets dissolve as double sulphurets of GOLD, PLATINUM,
ANTIMONY, TIN, ARSENIC, with SULPHURET OF AMMONIUM, or
POTASSIUM, and re-precipitate from their solution, upon the addi-
tion of an acid, either unaltered, or as regards the proto-sulphuret
of tin, and the sulphuret of antimony, in a state of higher sulphu-
ration, (the proto-sulphuret of tin absorbs sulphur from the
hydrosulphuret of ammonia.) The rationale of this precipitation
is as follows :—The acid decomposes the sulphur salt formed. The
sulphur base (sulphuret of ammonium or sulphuret of potassium)
transposes with the constituents of the water, to an oxygen base
(oxide of ammonium or potassa) and sulphuretted hydrogen ; the
former combines with the acid added, the latter escapes, and the
liberated electronegative sulphuret precipitates. (If the acid is an
hydracid, the radical combines with the ammonium and the hydro-
gen with the sulphur.) Sulphur precipitates at the same time, the
hydrosulphuret of ammonia in general containing an excess of
sulphur. The analyst must bear in mind that the thus eliminated

sulphur makes the color of the precipitated sulphurets appear lighter than they are naturally.

The alkalies, the alkaline earths, alumina, and oxide of chromium have remained in solution, because either their sulphur compounds are soluble in water, or their salts are not at all affected by sulphuretted hydrogen ; the sulphurets corresponding to the oxides of the fourth group, are insoluble in water, and would have been precipitated accordingly by sulphuretted hydrogen, but for the free acid present. If, therefore, this free acid be removed, i. e. if the solution be made alkaline, and then treated with sulphuretted hydrogen, or what answers both purposes at once, if

4. *Hydrosulphuret of ammonia*

be added to the solution, the sulphurets corresponding to the oxides of the fourth group will precipitate, viz. : SULPHURET OF IRON, SULPHURET OF MANGANESE, SULPHURET OF COBALT, SULPHURET OF NICKEL, and SULPHURET OF ZINC. Together with these sulphurets, ALUMINA, OXIDE OF CHROMIUM, and PHOSPHATE OF LIME, are thrown down, because the affinity which the oxide of ammonium possesses for the acid either of the salt of alumina and of oxide of chromium, or for that which keeps the phosphate of lime in solution, induces the elements of the hydrosulphuret of ammonia, to transpose with those of the water, thus giving rise to the formation of oxide of ammonium and of sulphuretted hydrogen. The former combines with the acid, the latter escapes, being incapable of entering into combination with the liberated oxides, or with the phosphate of lime,—the oxides and the lime-salt precipitate. There remain now in solution only the alkaline earths and the alkalies. The neutral carbonates of the former are insoluble in water, whilst those of the latter are soluble in that menstruum. If, therefore, we add now

5. *Carbonate of ammonia,*

and apply heat, in order to decompose the bicarbonates which may

have been formed, the whole of the alkaline earths ought to precipitate. This is, however, the case only as regards BARYTA, STRONTIA, and LIME ; of magnesia we know that, owing to its disposition to form double compounds with ammoniacal salts, it precipitates only in part; and that the presence of additional ammoniacal salts prevents its precipitation altogether. To prevent any uncertainty arising from this, chloride of ammonium is previously added to the carbonate of ammonia, and thus the precipitation of the magnesia is prevented altogether.

We have now in solution, magnesia, and the alkalies; the simple detection of magnesia may be effected by means of phosphate of soda and ammonia ; but its separation requires a different method, since the presence of phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesia is based upon the insolubility of magnesia in the pure state. The substance under examination is accordingly ignited in order to expel the ammoniacal salts, and the magnesia is then precipitated by means of baryta, the alkalies, the new-formed salt of baryta, and the excess of the caustic baryta added, remaining in solution. By the addition of carbonate of ammonia the whole of the baryta is removed from the solution which now contains the fixed alkalies, the ammoniacal salt formed, and the excess of the carbonate of ammonia added.

The ammoniacal salts are then removed by evaporating the solution to dryness and igniting the residue; the ignited residue consists of the fixed alkalies alone, or contains only a trace of carbonate of baryta arising from the circumstance of that substance not being entirely insoluble in a solution of chloride of ammonium or other ammoniacal salts, but which remains undissolved on the addition of water. This method of separating the baryta has the advantage over that of effecting the removal of this earth by means of sulphuric acid, that the alkalies are obtained in the most convenient form for their subsequent individual detection and isolation, viz., as chlorides.

The detection of the ammonia requires, of course, a fresh sample of the substance under examination.

b. DETECTION OF THE ACIDS.

Before passing over to the examination for acids and electro-negative substances, the analyst has to consider, in the first place, the nature of the detected bases, and the class to which the substance under examination belongs with respect to its solubility in water, or acids, since he can infer from these considerations which of the acids, and electro-negative bodies *may*, and *which cannot*, be present, and thus save himself the trouble of making unnecessary experiments. I refer the student, upon this point, to the table which will be found in the appendix, and in which the various compounds are arranged according to their several degrees of solubility in water, and acids. The general reagents applied for the detection of the acids are, for the inorganic acids, CHLO-RIDE OF BARIUM, and NITRATE OF SILVER, for the organic acids, CHLORIDE OF CALCIUM, and PERCHLORIDE OF IRON. It is therefore indispensable that the analyst should first assure himself whether he has to operate upon a substance containing inorganic acids alone, organic acids alone, or both together. In the examination for bases, the general reagents serve to effect the actual separation of the several groups of bases from one another; but in the examination for acids, they serve simply to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose we have an aqueous solution containing the whole of the acids in combination with soda, for instance.

Baryta forms insoluble compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boracic acid, chromic acid, oxalic acid, tartaric acid, and citric acid; these compounds are soluble in hydrochloric acid, with the exception of sulphate of baryta. If therefore to a portion of a neutral or alkaline solution, we add

1. *Chloride of barium,*

the formation of a precipitate will denote the presence of at least one of these acids. Upon treating the precipitate formed with

hydrochloric acid, the occurrence of a residue will at once denote the presence of sulphuric acid, since all the salts of baryta are soluble in this menstruum, with the exception of the sulphate. When sulphate of baryta is present, the reaction with chloride of barium fails to effect the positive detection of the whole of the other acids enumerated. For upon filtering the hydrochloric solution of the precipitates and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, &c., of baryta do not precipitate again, being kept in solution by the chloride of ammonium formed. Chloride of barium, therefore, cannot serve to effect the actual separation of the several acids from one another, and with the exception of sulphuric acid, is of no use for their individual detection. It is, however, of great importance as a reagent, since the non-formation of a precipitate upon its application to neutral or alkaline solutions, proves at once the absence of a considerable number of acids.

The compounds of silver, with chlorine, iodine, bromine, and cyanogen ; and of the oxide of silver, with phosphoric acid, arsenious acid, arsenic acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid, are insoluble in water. The whole of these compounds are soluble in ammonia, with the exception of iodide of silver, and in nitric acid, excepting the iodide, chloride, bromide, and cyanide of silver. If, therefore, we added to our solution which, for the reason just now stated, must be perfectly neutral,

2. *Nitrate of silver,*

and precipitation ensues, it proves at once the presence of one or several of the acids enumerated ; chromic acid, arsenic acid, and several others, of which the silver salts are colored, may even from this circumstance be individually recognized with a certain degree of safety. Upon treating the precipitate with nitric acid, the haloid compounds, if present, become manifest, since these remain undissolved, whilst the whole of the salts of the oxide dissolve. Nitrate of silver fails to effect the complete separation

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of those acids which form insoluble compounds with oxide of
silver, from the same cause which renders the separation of acids
by chloride of barium uncertain, viz. the ammoniacal salt formed
prevents the reprecipitation by ammonia, of several of the salts of
silver, from the acid solution.   Nitrate of silver, besides effecting
the separation of chlorine, iodine, bromine, and cyanogen, and
indicating the presence of chromic acid, &c., serves, like the
chloride of barium, to demonstrate at once the absence of a great
many acids, when it causes no precipitate in neutral solutions.
The deportment which the solution under examination exhibits
with chloride of barium, and with nitrate of silver, indicates, at
once, the further course of the investigation.   Thus, for instance,
if chloride of barium has produced a precipitate, whilst nitrate of
silver has failed to do so, it is not necessary to test for phosphoric
acid, chromic acid, boracic acid, silicic acid, arsenious acid,
arsenic acid, oxalic acid, tartaric acid, and citric acid, provided
always the solution contains no ammoniacal salts.   The same is
the case if we obtain a precipitate by nitrate of silver, but none
by chloride of barium.   Returning to our first supposition, viz.,
that the whole of the acids are present in the solution under
examination, we have now detected CHLORINE, BROMINE, IODINE,
and CYANOGEN, (for the separation and individual detection of
these substances, I refer to § 101.   Recapitulation and remarks,)
as also SULPHURIC ACID, and wehave reason to test for all the other
acids precipitated by these two reagents.   The detection of these
acids is based upon the results of a series of special experiments,
which have already been fully described and explained in the
course of the present work : the same remark applies to the rest
of the inorganic acids, and to nitric acid, and chloric acid.

   Of the organic acids, oxalic acid, tartaric acid, * and paratar-
taric acid, are precipitated by chloride of calcium, from aqueous
neutral solutions, in the cold, even though sal ammoniac be
present ; but the precipitation of citrate of lime is prevented by
the presence of ammoniacal salts, and ensues only upon ebullition
or mixing the solution with alcohol ; alcohol serves also to effect

   * The tartrate of lime separates only after the lapse of some time.

the separation of malate of lime from aqueous solutions. Accordingly upon adding to our solution,

3. *Chloride of calcium* and sal ammoniac,

OXALIC ACID, TARTARIC ACID, and PARATARTARIC ACID are precipitated, but the lime-salts of several inorganic acids, which have not yet been separated, (phosphate of lime for instance,) precipitate with lime-salts of organic acids. We must therefore select, for the individual detection of the precipitated organic acids, such reactions only as do not admit the possibility of confounding the organic, with the inorganic acids in admixture, which have likewise precipitated. For the detection of oxalic acid we select solution of sulphate of lime with acetic acid (§ 99. *c.* 5); to effect the detection of tartaric, and paratartaric acid, we treat the precipitate produced by chloride of calcium with solution of potassa, since the lime-salts of these two acids only are soluble in this menstruum in the cold, whilst the whole of the other insoluble lime-salts remain unacted on.

Of the organic acids we have now still in solution citric acid and malic acid, succinic acid and benzoic acid, acetic acid and formic acid. CITRIC ACID and MALIC ACID precipitate upon addition of alcohol to the fluid filtered from the oxalate, tartrate, &c., of lime, and which still contains an excess of chloride of calcium. Sulphate and borate of lime invariably precipitate with the malate and citrate of lime, if sulphuric acid and boracic acid happen to be present; we must therefore carefully guard against confounding the lime precipitates of these acids with those of citric acid and malic acid. The alcohol is now removed by evaporation, and

4. *Perchloride of iron*

added. This reagent precipitates SUCCINIC ACID and BENZOIC ACID in combination with peroxide of iron, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods which serve to effect the separation of the several groups from one another,

and the individual detection of the various acids, have been fully described and explained in the former part of this work.

B. SPECIAL REMARKS AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

To § 117.

At the commencement of § 117, the analyst is directed to mix neutral, or acid aqueous solutions, with hydrochloric acid. This acid is to be added drop by drop. If no precipitate forms, a few drops are sufficient, since the only object in that case is, to acidify the fluid in order to prevent the subsequent precipitation of the metals of the iron group, by sulphuretted hydrogen; the addition of the hydrochloric acid is to be continued, if a precipitate is formed, until this ceases to increase, and the fluid has acquired a distinctly acid reaction. Instead of this method of proceeding, some chemists have proposed to acidify a fresh sample of the solution under examination, with nitric acid. However, disregarding even the fact that nitric acid also produces precipitates in many cases, (in solution of potassio-tartrate of antimony, for instance), I prefer the use of hydrochloric acid, for the following reasons :— 1. Metals are more readily precipitated by sulphuretted hydrogen, from solutions acidified with hydrochloric acid, than from those acidified with nitric acid ;—2. In cases where the solution contains silver, protoxide of mercury, or lead, the further analysis is materially facilitated by the total, or partial precipitation of these three metals in the form of chloride ;—and 3. This form is the best adapted for the individual detection of these three metals when present in the same solution. Besides, the application of hydrochloric acid saves the necessity of examining whether mercury, which may be subsequently detected with the other metals of the fifth group, was originally present in the form of peroxide, or of protoxide. That the analyst obtains part of the lead in the form of a chloride, and the rest in the precipitate produced by sulphuretted hydrogen in the acidified solution, can hardly be thought an objection to the

application of this method, since he may, of course, omit the further examination for lead, on detecting this metal in the precipitate produced by hydrochloric acid.

A basic salt, of antimony, for instance, may be separated by the hydrochloric acid from potassio-tartrate of antimony, or some other analogous compound, and precipitate in conjunction with the insoluble chloride of silver and mercury, and the sparingly soluble chloride of lead. This precipitate, however, is readily soluble in the excess of hydrochloric acid which is subsequently added, and exercises therefore no influence whatever upon the further process. The application of heat to the acidified fluid is neither necessary, nor even advisable, since it might cause the conversion of a little of the precipitated protochloride of mercury into bichloride. Should bismuth, or chloride of antimony be present, the addition of the water, used to wash the precipitate produced by the hydrochloric acid, to the first filtrate, causes turbidity if the amount of free hydrochloric acid present is not sufficient to prevent the separation of the basic salt. This turbidity exercises, however, no influence upon the further process, since sulphuretted hydrogen as readily converts these finely-divided precipitates into sulphurets, as if the metals were in actual solution. In the case of alkaline solutions, the addition of hydrochloric acid is to be continued until the fluid acquires a strongly acid reaction. The hydrochloric acid neutralizes the substance which causes the alkaline reaction of the fluid, and the bodies which may be dissolved in, and combined with it, separate. If the alkali was present in a free state, oxide of zinc, for instance, or alumina, &c., may precipitate. But these oxides redissolve in an excess of hydrochloric acid ; chloride of silver, on the contrary, would not redissolve, and chloride of lead only with difficulty. If a metallic sulphur salt happen to be the cause of the alkaline reaction, the electro-negative sulphuret (e. g. sulphuret of antimony) precipitates upon the addition of hydrochloric acid ; whilst the electro-positive sulphuret (e. g. sulphuret of sodium) transposes with the constituents of hydrochloric acid to chloride of sodium and sulphuretted hydrogen. If an alkaline carbonate, a cyanide, or an alkaline sulphuret, happen to be the

cause of the alkaline reaction, carbonic acid, hydrocyanic acid, or sulphuretted hydrogen escape. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of certain groups of bodies.

To § 118.

I have already had occasion to remark, that upon adding a reagent (e. g. sulphuretted hydrogen) to a fluid under examination, precipitation *may* or may *not* ensue. The precipitate (produced, by sulphuretted hydrogen, for instance,) may be *white, yellow, orange, brown,* or *black.* Every one of these several cases is a different answer returned to the question which the analyst has put by means of the reagent, and every one of these replies has a different meaning. Correct observation, accurate apprehension, and a clear distinction of the several cases, is, therefore, indispensable. A mistake in this respect leads to fallacious results.

The color of the precipitate is almost invariably pointed out as a criterion in the systematic course of analysis. We may presume that a darker precipitate will sometimes conceal one of a lighter color, e. g. that a precipitate of black sulphuret of mercury may conceal from view a precipitate of yellow sulphuret of arsenic ; and on the other hand, we may conclude, that a light-colored precipitate cannot hide one of darker hue, and thus, for instance, that a white precipitate cannot conceal a black one. Conclusions of this kind cannot, however, always be drawn with the same degree of positive certainty, since few colors offer the pointed contrast of black and white, and many of them rather merge into each other, e. g. yellow and orange. In all cases where the indications afforded by the color of a precipitate are at all doubtful, it is advisable to pursue that course which the darker of the colors in question indicates, since this comprises the whole of the metals which can possibly have precipitated, whilst the other excludes the precipitates of darker color. The most comprehensive course is invariably the best, although it may be the most protracted and circuitous.

A judicious distribution, and economy of time is especially to be studied in the practice of analysis; many of the operations may be carried on simultaneously, which the student will readily perceive and arrange for himself.

In cases where the analyst has simply to deal with metallic exides of the sixth group, (e. g. oxide of antimony,) and of the fourth group, (e. g. the oxides of iron,) he need not precipitate the acidified solution with sulphuretted hydrogen, but may, after neutralization, at once add hydrosulphuret of ammonia in excess. The sulphuret of iron, &c., will in that case precipitate, whilst the antimony, &c., will remain in the solution, from which they will, upon addition of an acid, at once be thrown down as sulphuret of antimony, &c. This method has the advantage of rendering the fluid less dilute than is the case when sulphuretted hydrogen is used, and moreover of facilitating and accelerating the operation. Finally, once more I must remind the student that the perfect purity of the reagents, and their application in correct quantity, rank amongst the most indispensable conditions of successful analysis. This applies more particularly to sulphuretted hydrogen, especially when used in the gaseous form. In such cases, students often lose sight of the circumstance that sulphuretted hydrogen gas fails to precipitate highly acid solutions unless they be previously diluted with water.

To § 119.

The digestion of the precipitates which sulphuretted hydrogen has thrown down from acid solutions requires above all that the digesting agent (the hydrosulphuret of ammonia) be applied in correct proportion. A small quantity is generally sufficient, but should protosulphuret of tin be present, a somewhat larger amount is required. Inexperienced students, however, frequently use so much of it that, upon the addition of an acid, sulphur separates to such an amount that the color of the precipitated sulphuret is quite obscured and concealed by it. The separation and individual detection of antimony, tin, and arsenic, is not a very easy task, if these three metals have been precipitated together as sulphurets. Beginners will find it difficult to distinguish between

them before the below-pipe. The method of separation given in
§ 119, and which when carefully executed may be entirely de-
pended on, is explained in the following manner :—

When the sulphurets of arsenic, tin, and antimony are defla-
grated with a mixture of nitrate and carbonate of soda, the me-
tals, and the sulphur are oxidized at the expense of the nitric
acid. The fused mass contains arseniate, antimoniate, and sul-
phate of soda, with oxide of tin, besides the excess of nitrate and
carbonate of soda. Now, on treating this with cold water, the
arseniate, and sulphate of soda dissolve, whilst the antimoniate of
soda, and oxide of tin are unacted on, or nearly so. By using a
mixture of alcohol, and water to wash the residue, the decomposi-
tion of the antimoniate of soda is prevented.

When the alkaline solution is neutralized with nitric acid it
generally becomes slightly turbid, owing to the separation of a
trace of hydrated antimonic acid, and oxide of tin. If arsenic is
present the precipitate is not quite free from it. Thus it is ob-
vious that care must be taken to avoid the presence of much anti-
moniate, or stannate of soda in the solution, and for this reason
the deflagrated mass is exhausted with cold, instead of hot water.
In the solution, neutralized or slightly acidified with nitric acid,
there exists, after filtration, arseniate and sulphate of the alkali.
One portion of this liquid is to be precipitated with nitrate of
silver and ammonia, according to § 119.; the other with solution
of acetate of lead. To detect the arseniate of silver the solution
must be quite neutral, and as this is not always easy to effect, the
slightly acid liquid, to which the solution of silver has been added,
is to be lightly covered with a weak solution of ammonia. This
is the most efficient method of producing a precipitate when only
small quantities of arsenic are present. By the precipitation with
acetate of lead, a mixture of sulphate, and arseniate of lead is
obtained.

The sulphate of lead increases the bulk of the precipitate, and
thus renders its collection, and subsequent examination a task
of greater facility than would be the case if only the arseniate of
lead were present; as from the increased size of the button, the
arsenical vapors can be produced, even after repeated fusions before

the blow-pipe. Although these reactions may be considered fully to demonstrate the presence of arsenic, yet the production of an arsenical mirror is, after all, indispensable on important occasions.

If, after treating the deflagrated mass with water, the residue, which consists of antimoniate of soda, and oxide of tin, be boiled with a solution of caustic potassa, or soda, and then some alcohol added, the antimoniate of soda will remain entirely undissolved, whilst the oxide of tin as a stannate of the alkali will be found in the solution. As by this means a sufficient separation of the two metals is effected, the recognition of each individually presents no difficulty.

To § 120.

By heating the sulphurets of the second section of the fifth group, to the examination of which we now proceed, with nitric acid to the boiling point, lead, bismuth, copper, and cadmium will be oxidized at the expense of one portion of the nitric acid, which is resolved into nitric oxide, and oxygen, whilst the sulphur is precipitated, and the oxides combining with the remaining nitric acid form soluble nitrates.

Sulphate of mercury, on the other hand, is not decomposed by nitric acid unless a chloride be present, owing to imperfect washing.

The separation of the four metals in the solution is effected simply as follows : it is only with lead that sulphuric acid forms an insoluble compound ; if therefore sulphuric acid be added to the nitric acid solution, lead will be separated. Oxide of bismuth is insoluble in ammonia, whilst oxides of copper and cadmium dissolve in that menstruum. On the addition of ammonia in excess to the solution filtered from sulphate of lead, the oxide of bismuth precipitates, and the oxides of copper and cadmium remain dissolved ; the former of these is recognized by the blue color imparted to the liquid. These two oxides are separated by means of carbonate of ammonia ; after neutralizing the ammoniacal liquid with hydrochloric acid and concentrating by evaporation, an excess of carbonate of ammonia solution is added, in which oxide of cadmium is insoluble. As regards the further

determination of the separate oxides a special theoretical explanation is necessary.

Besides the methods just given to distinguish between cadmium, copper, lead, and bismuth, the following yields very satisfactory results. Carbonate of potassa is added to the nitric acid solution as long as a precipitate continues to form; solution of cyanide of potassium in excess is then added, and heat applied. This effects the complete separation of lead, and bismuth in the form of carbonates, whilst copper, and cadmium are obtained in solution as the double cyanides of copper, and potassium, and cadmium, and potassium. Lead, and bismuth may now be readily separated from one another by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in cyanide of potassium, sulphuretted hydrogen in excess, applying heat, and subsequently adding some more cyanide of potassium, in order to redissolve the sulphuret of copper, which may have precipitated with the sulphuret of cadmium. A yellow precipitate (sulphuret of cadmium) which is insoluble in cyanide of potassium, demonstrates the presence of cadmium. The fluid is filtered from this precipitate, and hydrochloric acid added to the filtrate; when the formation of a black precipitate (sulphuret of copper) will demonstrate the presence of copper. The presence of mercury might indeed be considered sufficiently proved by the black residue which remains upon treating the sulphuret with nitric acid. The eliminated sulphur, however, frequently envelops small particles of the other black sulphurets, and appear for this reason black here and there, and also in some instances heavy, from a mixture of sulphate of lead, (formed by the action of the nitric acid upon the sulphuret of lead). It is therefore indispensable to subject every residue remaining upon ebullition with nitric acid to further examination, unless it consists of pure yellow sulphur, which mostly floats upon the fluid. The test with clean copper is most convenient and expeditious. I have to remark, however, that the application of this test more frequently gives rise to fallacious results than the reaction with protochloride of tin. With regard to the latter, it is indispensable that the reagent be pure, and that

the solution of mercury no longer contain any nitric acid. If the protoxide of mercury has first been separated by hydrochloric acid, the precipitate of sulphuret of mercury which forms upon the addition of sulphuretted hydrogen, invariably corresponds to the peroxide, perchloride, &c. of mercury. If the analyst has to deal with an aqueous solution, or with a solution in very dilute hydrochloric acid, he may consider that the mercury was originally present in the analysed substance, in the form of peroxide, perchloride, &c. : but in the case of a nitric acid solution, the mercury can have existed originally as protoxide, and subsequently acquired a higher degree of oxidation.

To § 121.

The precipitate produced by hydrosulphuret of ammonia may, as already stated, consist of sulphurets, of oxides, and of the phosphates of the alkaline earths, phosphate of alumina, oxalate of lime, (baryta and strontia,) as well as the fluorides of the metals and alkaline earths. The borates of the alkaline earths and the oxalate of magnesia would, also, precipitate, were they not retained in solution by the chloride of ammonium formed in the fluid, or added to it. It is a matter of perfect indifference, as regards the final results of this operation, whether, upon the simple addition of ammonia, a precipitate forms or not, since hydrosulphuret of ammonia decomposes the recently precipitated hydrated oxides of iron, &c. without difficulty. Nor can any positive inference respecting the presence, or absence of certain metals and compounds be drawn from this reaction, unless the sulphuretted hydrogen be previously altogether removed from the fluid, and the absence of organic matter insured. In § 121, we have two distinct cases, of which the first (formation of a white precipitate) requires no further explanation, especially as it is included in the second, (formation of a dark colored precipitate). We therefore proceed at once to the mode of treatment which is to be adopted, when all the substances now under consideration are contained in the hydrosulphuret of ammonia precipitate. From these, however, we may except chromium, and the more readily, as the separation of chromium by fusion with nitrate of potassa, and soda is a very

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characteristic test, and an operation easily understood. We will therefore suppose the precipitate to contain : sulphurets of cobalt, nickel, iron, manganese, and zinc, together with alumina (phosphate) and phosphate of lime.

The sulphurets of cobalt, and nickel are difficultly soluble in cold dilute hydrochloric acid, whilst the other bodies readily dissolve in it. Therefore, on treating the precipitate with this reagent, the two first-mentioned substances remain almost unacted on, whilst the last five will entirely dissolve, together with traces (only) of cobalt and nickel.

If the solution, after boiling to free it from sulphuretted hydrogen, be treated with excess of solution of caustic soda, the oxide of zinc and alumina (phosphate) remain in solution ; the other bases are insoluble, the iron as the black proto and peroxide, in which state it is most easily separated from alumina; a small portion of the oxide of zinc is always found in the precipitate. The residue, after small portions have been tested for iron, and manganese, is to be dissolved in hydrochloric acid, and in order to obtain the iron entirely as protoxide, the solution must be treated with sulphite of soda, and then decomposed with acetate of soda. The solution is still clear ; it contains, at least we may suppose it to be so, protoxide of iron and manganese, as well as traces of protoxide of cobalt and nickel, and oxide of zinc combined with acetic acid, added to which phosphate of lime is dissolved by the excess of acetic acid and chloride of sodium, which results from the combination of the hydrochloric acid, that had previously been the metallic solvent, with the soda of the acetate of soda. On the addition of perchloride of iron, decomposition ensues, chloride of calcium, and perphosphate of iron being formed, the latter of which is insoluble in acetic acid, or proto-acetate of iron, and separates as a yellowish-white precipitate. If chloride of iron be added until from the formation of peracetate of iron the liquid begins to change to a deep red color, we may rest assured that all the phosphoric acid has separated in combination with only a slight excess of oxide of iron. Had we not reduced the solution before adding the acetate of soda, the latter would have changed the liquid to a deep red, from the formation of peracetate

of iron, in which perphosphate of iron is soluble to a considerable extent, consequently if only a small portion of phosphoric acid were present we should fail to detect it; and on boiling the liquid the phosphoric acid would be thrown down with a large excess of peroxide of iron, and the recognition of it in the precipitate be rendered more difficult.

All the phosphoric acid is now precipitated in combination with the oxide of iron, the filtrate containing the substances before mentioned. The addition of ammonia, and hydrosulphuret of ammonia precipitates all the heavy metals, whilst the lime (and in general the alkaline earths that had existed in combination with the phosphoric acid) remains dissolved, and may be detected in the usual way. By dissolving the metallic sulphuret in hydrochloric acid, (by which, again, a trace of sulphuret of cobalt and nickel may possibly remain undissolved,) then boiling with nitric acid, nearly neutralizing with carbonate of soda, and decomposing with carbonate of baryta,-all the oxide of iron will precipitate as a basic salt, and the solution, after throwing down the baryta with sulphuric acid, can easily be tested for the smallest portion of zinc, cobalt, and nickel.

To § 130.

The third class of substances has no strictly definable limits, as the solubility, or insolubility of several compounds belonging to it depends very much upon the quantity, and concentration of the acid, and the time of boiling. Besides the difficultly soluble substances enumerated, the analyst has to look particularly for many metallic sulphurets, and iodides, which dissolve only upon continued boiling in concentrated hydrochloric acid. If a substance dissolves in nitric acid, upon long protracted ebullition, the analyst must not conclude, that protochloride of mercury is absent, since this substance, as I have already stated, is converted in this process into pernitrate of mercury, and perchloride of mercury, and thus dissolved.

Chloride of silver, protochloride of mercury, and chloride of lead may have been present in the original compound in the form of chloride, or may have been converted into this form by the hydro-

chloric acid. The presence of the chloride of lead has in that case been already detected in the aqueous solution. Whether the two other chlorides were originally present in that form, may be ascertained in the following manner :—The substance insoluble in water is treated with dilute nitric acid. This effects the solution of the whole of the salts of protoxide of mercury and oxide of silver, whilst the above enumerated chlorides, and the iodide of silver remain undissolved. These are then separated by means of ammonia, which serves at the same time to effect the detection of the protochloride of mercury.

The decomposition of the sulphates of the alkaline earths may also be effected in the humid way by protracted boiling with solution of carbonate of potassa. But the fusion with carbonate of potassa and soda, yields far safer results, and is moreover very expeditious when operating upon small quantities. This method has also this advantage over the decomposition in the humid way, that it leads to the positive detection of the presence of silicic acid.

The sulphates of the alkaline earths are decomposed by the alkaline carbonates in such a manner that carbonates of the alkaline earths, and sulphate of the alkali are formed. If the precipitate of the former be not thoroughly washed, previously to its solution in hydrochloric acid, sulphates of the alkaline earths will again be formed by the action of the alkaline sulphate which still adheres to the precipitate; this would tend to vitiate the results of the experiment, since, for instance, all the baryta dissolved might re-precipitate.

Carbon has been connected with this third class, since it sometimes occurs in the course of the examination, and may thus become a great obstacle to the progress of the inexperienced student, should he be unprepared for its presence. Graphite is distinguished from the other forms of carbon by its difficult combustion before the blow-pipe, and its non-combustion in a platinum spoon; besides these indications, the iron, which graphite generally contains in admixture, denotes its presence.

To § 181.

The analysis of cyanogen compounds is not very easy in certain

cases, and it is sometimes extremely difficult to ascertain whether we have really a cyanide before us or not. If, however, the phenomena which the substance under examination manifests upon ignition, (§ 107. A. I. 2. (3,) be carefully observed, and also, whether upon ebullition with hydrochloric acid any odor of hydrocyanic acid is emitted, (§ 109. A. 2. (35,) the presence, or absence of a cyanide will not long remain a matter of doubt.

It must now above all be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two distinct classes. They are either SIMPLE CYANIDES, or COMPOUNDS OF METALS WITH FERROCYANOGEN, or with some other analogous compound radical.

All the simple cyanides are decomposed upon boiling with concentrated hydrochloric acid, into metallic chlorides and hydrocyanic acid. Consequently their analysis is never difficult. But the ferrocyanides, &c., (to which the method described at § 131. refers indeed exclusively,) undergo by acids such complicated decompositions that their analysis in this manner is a task not so easily accomplished. Their decomposition by potassa is far more simple. The potassa yields its oxygen to the metal combined with the ferrocyanogen, &c., the oxide precipitates, and the reduced potassium forms soluble ferrocyanide, &c. of potassium with the liberated radical. But several oxides are soluble in an excess of potassa, such as oxide of lead, oxide of zinc, &c. If, therefore, the double ferrocyanide of zinc and potassium, for instance, be boiled with solution of potassa, it will completely dissolve in that menstruum.

Were we to add an acid to this solution, we should simply reobtain our original precipitate of the double ferrocyanide of zinc and potassium, and our experiment would consequently be of no avail. To prevent this, we transmit sulphuretted hydrogen through the solution. This converts the whole of the heavy metals which the potassa contains in solution as oxides, into sulphurets. Those sulphurets which are insoluble in potassa, such as sulphuret of lead, sulphuret of zinc, &c. precipitate, whilst those which are soluble in alkaline sulphurets, such as sulphuret of tin, sulphuret of antimony, &c., remain in solution, but are precipitated upon the addition of an acid.

The fluid filtered from the precipitated oxides or sulphurets, invariably contains the cyanogen as ferrocyanide, &c., of potassium, (provided, of course, the analysed compound really consist of a double ferrocyanide, &c., &c.) From most of the compounds (ferrocyanide, ferricyanide, chromicyanide, and manganocyanide of potassium) the cyanogen partly separates as hydrocyanic acid, upon boiling the solution with sulphuric acid, and may thus be readily detected. But the cobalticyanide of potassium is not decomposed by sulphuric acid, and this renders the *direct* demonstration of the presence of cyanogen in this double compound a difficult task. Upon fusion with nitrate of potassa, the whole of these double compounds suffer decomposition, cobalticyanide of potassium •not excepted. The reason why the fusion of these double compounds with nitrate of potassa is to be preceded by evaporation with an excess of nitric acid, is simply to prevent the occurrence of explosion. Caution is highly advisable in this operation. If the analyst merely wishes to detect the bases in simple or double cyanides, he may in most cases accomplish his object by igniting the substance under examination, or by fusing it with carbonate of soda and potassa. This process yields the metals either in the metallic state, or in combination with carbon. If the compound has been fused with the alkaline carbonates, cyanide of potassium is found in the slag, should this not have been converted into cyanate of potassa, owing to the adventitious presence of reducible oxides. (Vide § 101. *d.* 2.)

APPENDIX.

I.

§ 134.

DEPORTMENT OF THE MOST IMPORTANT OF THE ALKALOIDS WITH REAGENTS.

A SYSTEMATIC METHOD OF EFFECTING THE DETECTION OF THESE SUBSTANCES.

The detection, and separation, of the alkaloids is a task of far greater difficulty than that of most of the inorganic bases. Although the difficulty is owing partly to the circumstances that scarcely one of the compounds which the alkaloids form with other substances, is perfectly insoluble or particularly characterized by its color or any other salient property, yet the principal cause of this difficulty must be ascribed to the want of accurate and minute investigations of the salts and other compounds of the alkaloids, together with the products of their decomposition. For this reason, although acquainted with the reactions, we cannot conceive the causes of, and consequently understand, the conditions which may tend to modify them.

Now although, in the present imperfect state of our knowledge of these bodies, an attempt to define their deportment with reagents, and base thereon a method of effecting their separation, or, at least individual detection, must of necessity fall very short

* The reader will observe that some of the formulæ in the following pages, differ from those usually adopted in this country, but as the results are the same, it has been deemed best to adhere to the German text.

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of perfection, yet, having made a great many experiments on the
nature and behaviour of these substances, I will attempt here, for
the benefit of young chemists, and more particularly pharmaceu-
tists, to describe in some measure the reactions which the most
important of the alkaloids manifest with other bodies, and to lay
down a systematic method of effecting their individual detection.

The classification of the alkaloids into groups which I have
adopted here, is based upon their deportment with certain general
reagents.   I have verified by numerous experiments the whole of
the reactions described in the succeeding paragraphs.

<div align="center">FIRST GROUP.</div>

<div align="center">§ 135.</div>

ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE
SOLUTIONS OF THEIR SALTS, AND REDISSOLVE IN AN EXCESS OF
THE PRECIPITANT. Of the alkaloids of which I purpose to treat,
one only belongs to this group, viz.,

<div align="center">MORPHIA ($C_{35} H_{20} N O_6 = \overset{+}{Mo}$)</div>
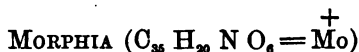
1. Morphia usually appears in the form of colorless, brilliant,
four-sided prisms or, upon precipitation from the solution of its
salts, as a white powder composed of crystalline flakes. It has a
bitter taste, and dissolves very sparingly in cold, but somewhat
more readily in boiling water. Of cold alcohol, it requires ninety
parts by weight for solution ; of boiling alcohol, from twenty to
thirty parts. The solutions of morphia in alcohol, and hot water
manifest distinctly alkaline reactions. This alkaloid is insoluble
in ether.

2. Morphia neutralizes acids completely, and forms with them
the SALTS OF MORPHIA. These salts are readily soluble in water,
and spirits of wine, but are insoluble in ether ; their taste is bitter
and disagreeable. Most of them are crystallizable.

3. *Potassa*, and *ammonia* precipitate morphia from the solutions
of its salts, in the form of a white crystalline powder. Stirring and
friction on the sides of the vessel promote the separation of the
precipitate, which redissolves with great readiness in an excess of

potassa, but with somewhat more difficulty in ammonia. The precipitated morphia is soluble in chloride of ammonium, and also, but with difficulty, in carbonate of ammonia.

4. *Carbonate of potassa, and carbonate of soda* produce the same precipitate as potassa, and ammonia, but fail to redissolve it upon addition in excess. Consequently if a fixed alkaline bicarbonate is added to a solution of morphia in caustic potassa, the morphia separates (especially after previous ebullition) in the form of a crystalline powder. A more minute inspection, especially through a magnifying glass, shews this powder to consist of small acicular crystals; seen through a glass which magnifies one hundred times, these crystals present the form of four-sided prisms.

5. *Bicarbonate of soda, and bicarbonate of potassa* precipitate morphia from the solutions of its neutral salts, in the form of a crystalline powder. The precipitate is insoluble in an excess of the precipitants. These reagents fail to precipitate acidified solutions of salts of morphia, in the cold.

6. The action of strong *nitric acid,* upon morphia, or one of its salts, in the solid state, or in concentrated solutions, produces a fluid varying from red to yellowish red. Dilute solutions do not change their color, upon addition of nitric acid, in the cold, but upon boiling they acquire a yellow tint.

7. *Neutral perchloride of iron* imparts to neutral solutions of salts of morphia a beautiful dark blue color, which disappears upon the addition of an acid. Should the solution contain admixture of animal, or vegetable extractive matter, or of acetates, the coloration will appear clouded and less distinct.

8. If *iodic acid* is added to a solution of morphia, or of a salt of morphia, IODINE separates. In aqueous, and concentrated solutions, the separated iodine appears as a kermes brown precipitate, whilst in alcoholic and dilute solutions it imparts a brown, or yellowish-brown color to the fluid. The addition of starch paste to the fluid heightens the delicacy of the reactions considerably, since the blue tint of the iodide of starch remains perceptible in exceedingly dilute solutions, which is not the case with the brown coloration imparted by iodine.

9. *Perchloride of gold* produces in concentrated solutions of salts of morphia a flocculent yellowish-grey brown precipitate, which redissolves in an excess of the precipitant, and also in hydrochloric acid to a green fluid. In dilute solutions the reagent produces simply a green coloration ; but in either case the fluid acquires a yellow tint, after standing for some time, and metallic gold separates in the form of a yellowish brown powder.

SECOND GROUP.

§ 136.

ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE, TO A PERCEPTIBLE EXTENT, IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY BICARBONATE OF SODA EVEN FROM ACID SOLUTIONS : Narcotina—Quina—Cinchonia.

$$a.\ \text{NARCOTINA}\ (C_{46}\ H_{25}\ N\ O_{14} = \overset{+}{N}a).$$
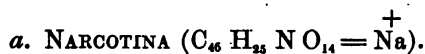
1. Narcotina appears usually in the form of colorless, brilliant, rhombic prisms, or, upon precipitation by alkalies, as a white loose crystalline powder. It is insoluble in water. Alcohol and ether dissolve it sparingly in the cold, but more readily upon heating. Solid narcotina is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotina does not alter vegetable colors.

2. Narcotina dissolves readily in acids, combining with them and forming salts. These salts have invariably an acid reaction. Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even upon simple evaporation. Most of the salts of narcotina are amorphous, and soluble in water, alcohol, and ether.

3. *Pure alkalies, alkaline carbonates,* and *bicarbonates* precipitate narcotina from the solutions of its salts, in the form of a white powder, which seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitant. If a solution of narcotina is mixed with ammonia, and ether added, the narcotina

which separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers.

4. *Concentrated nitric acid* dissolves narcotina to a colorless fluid, which acquires a pure yellow tint upon application of heat.

5. *Concentrated sulphuric acid* dissolves narcotina to a yellow fluid which turns brown upon application of heat. A solution of narcotina in concentrated sulphuric acid containing a *slight* admixture of nitric acid, appears of an intense blood-red color, which disappears altogether upon the addition of a somewhat larger amount of nitric acid.

6. If narcotina or one of its salts is dissolved in an excess of dilute sulphuric acid, some finely levigated peroxide of manganese added, the mixture heated to boiling, and maintained in ebullition for the space of several minutes, the narcotina absorbs oxygen and is converted into opianic acid, cotarnina (a base soluble in water) and carbonic acid.

$$b. \ \text{QUINA} \ (C_{20} \ H_{12} \ N \ O_2 = \overset{+}{Q}).$$

1. Quina appears either in the form of fine crystalline needles of silky lustre, which are frequently aggregated into tufts, or as a loose white powder. It is sparingly soluble in cold, but somewhat more readily in hot water. It is readily soluble in spirits of wine, both cold, and hot, but far less so in ether. The taste of quina is intensely bitter; the solutions of quina manifest alkaline reaction.

2. Quina neutralizes acids completely. The salts taste intensely bitter; most of them are crystallizable, and for the greater part readily soluble in water and spirits of wine.

3. *Potassa, ammonia,* and the neutral *carbonates of the alkalies,* produce in solutions of salts of quina (provided they be not too dilute) a white, loose, pulverulent precipitate of hydrated quina, which immediately after precipitation, appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of aggregated crystalline needles. The precipitate redissolves to a scarcely perceptible extent only, in an excess of potassa, but more readily in ammonia. It is hardly more soluble in fixed alkaline carbonates than in pure water. If

a solution of quina is mixed with ammonia, ether added, and the mixture shaken, the quinine which separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers.

4. *Bicarbonate of soda* also produces, and this both in neutral, and acid solutions of salts of quina, a white pulverulent precipitate of hydrated quina. From dilute solutions, the quina separates only *after the lapse of some time*, and appears in such cases in the form of white, and opaque needles aggregated into tufts. Vigorous stirring of the fluid promotes the separation of the precipitate considerably. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more perfect, the less the excess of the precipitant. From this solution in an excess of bicarbonate of soda, the quina precipitates upon protracted ebullition.*

5. *Concentrated nitric acid* dissolves quina to a colorless fluid, becoming yellowish upon the application of heat.

6. *Concentrated sulphuric acid* likewise dissolves pure quina and pure salts of quina to colorless fluids which do not acquire any coloration upon being heated to the point of incipient evaporation of the sulphuric acid, but afterwards they become yellow and finally brown. Sulphuric acid containing an admixture of nitric acid, dissolves quina to a colorless, or faint yellowish fluid.

$$c. \text{ CINCHONIA } (C_{20} H_{12} N O = \overset{+}{Ci}).$$

1. Cinchonia appears either in the form of pellucid, brilliant, four-sided prisms, of fine white crystalline needles, or when precipitated from concentrated solutions, as a loose white powder. Recently prepared, or precipitated, cinchonia is tasteless, but acquires, by keeping, the bitter taste of the bark. Cinchonia is

* A remark made by C. F. Oppermann (Considérations sur les Poisons Végétaux, Strasbourg, 1845) impeaching the correctness of my statement regarding the precipitation of a solution of quina acidified with sulphuric acid by bicarbonate of soda, induced me to repeat my former experiments, but invariably with the same results, viz. concentrated solutions were precipitated immediately, dilute solutions after the lapse of from two to fifteen minutes, this operation being greatly promoted by vigorous stirring of the fluid.

nearly insoluble in cold, and exceedingly difficult of solution in hot water; it is but slightly soluble in cold dilute spirits of wine, somewhat more so in hot spirits of wine, and most readily in absolute alcohol. From hot alcoholic solutions the greater portion of the dissolved cinchonia separates upon cooling. Solutions of cinchonia taste bitter, and manifest alkaline reaction. Cinchonia is insoluble in ether.

2. Cinchonia neutralizes acids completely. The salts have the bitter taste of the bark; most of them are crystallizable, and generally more readily soluble in water, and spirits of wine, than the corresponding quina compounds. Ether fails to dissolve them.

3. Cinchonia fuses when heated cautiously; subsequently white fumes arise, which, like benzoic-acid, condense upon cold substances, in the form of small brilliant needles, or as a loose sublimate. This sublimation of cinchonia is attended with emission of a peculiar aromatic odor.

4. *Potassa, ammonia,* and the *neutral carbonates of the alkalies* produce in solution of salts of cinchonia, a white, loose, precipitate of CINCHONIA, which does not exhibit a distinctly crystalline appearance even though viewed through a lens magnifying from 200 to 300 times. The precipitate does not redissolve in an excess of the precipitants.

5. *Bicarbonate of soda* and *bicarbonate of potassa* precipitate cinchonia in the same form as at 4. both from neutral and acid solutions, but not so completely as the carbonates of the alkalies. The bicarbonates accordingly fail to precipitate highly dilute solutions, and the fluid filtered off from the precipitate produced in more concentrated solutions, becomes turbid upon protracted boiling.

6. *Concentrated sulphuric acid* dissolves cinchonia to a colorless fluid which, upon application of heat, first acquires a brown, and finally a black color. Solution of cinchonia in concentrated sulphuric acid containing an admixture of nitric acid is equally colorless in the cold, but, upon application of heat, passes through the intermediate tints of yellow, red-brown, and brown, and finally turns black.

Recapitulation and Remarks.

The alkaloids of the second group are altered or precipitated by various other reagents besides those mentioned above; the reactions are, however, not adapted to affect their individual detection and separation. Thus, for instance, dilute solution of iodine produces in solutions of the salts of the three alkaloids belonging to this group, a *red-brown* precipitate, bichloride of potassium, *yellowish-white*, perchloride of mercury, *white*, perchloride of gold, *yellow*, nitrate of silver, with addition of ammonia to neutralization, *white*, tincture of galls, *yellowish-white flocculent* precipitates, &c.

Narcotina, and Quina being soluble in ether, whilst cinchonia is insoluble in that menstruum, they may be most readily separated by this means from the latter alkaloid. To effect their separation, the analyst need simply mix the solution of the three alkaloids with ammonia in excess, then add ether, and filter the solution of quina, and narcotina from the undissolved cinchonia. If the ether be then evaporated at a gentle heat, the ammonia being all the time maintained in excess, the narcotina will precipitate, and may be readily separated by filtration from the quina which remains in solution. The quina may then be precipitated from the solution by cautious neutralization of the ammonia with an acid, and finally recognized under the microscope, by the form of its crystals.

THIRD GROUP.

§ 137.

ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT, AND ARE NOT PRECIPITATED FROM ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALIES: Strychnia, Brucia, Veratria.

a. STRYCHNIA $(C_{44} \ H_{23} \ N_2 \ O_4 \overset{+}{=} Sr.)$

1. Strychnia appears either in the form of white, brilliant,

octohedrons, of four-sided prisms, or finally, when produced by precipitation, or rapid evaporation, as a white powder. It has an exceedingly bitter taste. It is nearly insoluble in cold, and scarcely soluble in hot water. It is insoluble in absolute alcohol and ether, and difficultly soluble in dilute spirits of wine. On heating it does not fuse.

2. Strychnia neutralizes acids completely. Most of the salts of strychnia are crystallizable, and soluble in water. All the salts of strychnia have an insupportably bitter taste, and are exceedingly poisonous.

3. *Potassa*, and *carbonate of potassa* produce in solutions of salts of strychnia white precipitates of strychnia, which are insoluble in an excess of the precipitants. Viewed through a lens, magnifying one hundred times, the precipitate appears as an aggregate of small crystalline needles. From dilute solutions the strychnia separates only after the lapse of some time, in the form of crystalline needles, which are perfectly visible even to the naked eye.

4. *Ammonia* produces the same precipitate as potassa. The precipitate redissolves in an excess of ammonia, but after a short time (or if the solution is highly dilute, after a more considerable lapse of time) the strychnia crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible to the naked eye.

5. *Bicarbonate of soda* produces in neutral solution of salts of strychnia, a precipitate of strychnia, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (so as to leave the fluid still alkaline) the precipitate dissolves readily in the liberated carbonic acid. The addition of bicarbonate of soda to acid solution of strychnia, causes no precipitation, and it is only after the lapse of twenty-four hours, or even a longer period, that strychnia crystallizes from the fluid in distinct prisms, and this crystallization continues in proportion as the free carbonic acid escapes. If a concentrated solution of strychnia, supersaturated with bicarbonate of soda, is boiled for some time, a

precipitate forms immediately ; from dilute solutions, this precipitate separates only after concentration.

6. The addition of an aqueous solution of *iodic acid* to solutions of salts of strychnia, produces no alteration in the cold ; but upon subsequent application of heat, the fluid turns VIOLET, and after the lapse of some time a blackish precipitate separates.

7. *Sulphocyanide of potassium* produces in concentrated solutions of salts of strychnia immediately, and in dilute solution, after the lapse of some time, a white crystalline precipitate, which appears under the microscope as an aggregate of flat needles, and is but little soluble in an excess of the precipitant.

8. On placing a drop of concentrated sulphuric acid on a watch-glass, and adding to it a little strychnia or a salt of strychnia, solution ensues without any particular reaction ; but on mixing a drop of solution of chromate of potassa with it, it instantly assumes a deep blue color which soon changes to red.

9. *Perchloride of mercury* produces, in solutions of salts of strychnia, a white precipitate, which changes after some time to crystalline needles aggregated into stars, and distinctly visible through a lens. Upon heating the fluid these crystals redissolve, and upon subsequent cooling of the solution, the double compound re-crystallizes in distinct needles.

10. *Concentrated nitric acid* dissolves strychnia, and its salts to colorless fluids, which become yellow upon the application of heat.

$$+$$

b. BRUCIA (C_{44} H_{25} N_2 O_7 = Br.)

1. Brucia appears either in the form of transparent, rhombic prisms, or in that of crystalline needles, aggregated into stars, or as a white powder composed of minute crystalline scales. Brucia is difficultly soluble in cold, but somewhat more readily so in hot water. Both absolute, and dilute alcohol dissolve it readily, but it is insoluble in ether. Its taste is intensely bitter.

2. Brucia neutralizes acids completely. The salts of brucia are readily soluble in water, and of an intensely bitter taste. Most of them are crystallizable.

3. *Potassa,* and *carbonate of potassa* throw down from solutions of salts of brucia a white precipitate of brucia, which is insoluble in an excess of the precipitant. Viewed under the microscope, immediately after precipitation, the precipitate appears to consist of very minute grains, but, upon further inspection, these grains are seen to form into needles, which latter subsequently arrange themselves into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. *Ammonia* produces a whitish precipitate in solution of salts of brucia, which appears at first like a number of minute drops of oil, but changes subsequently to small needles. The precipitate redissolves, immediately after separation, in an excess of the precipitant, but after a very short time (or, if the solution is highly dilute, after a more considerable lapse of time) the brucia crystallizes from the ammoniacal solution in small concentrically grouped. needles, which addition of ammonia fails to redissolve.

5. *Bicarbonate of soda* produces, in neutral solutions of salts of brucia, a precipitate of brucia, which separates after the lapse of a short time, in form of concentrically aggregated needles of silky lustre, which are insoluble in an excess of the precipitant, but dissolve in free carbonic acid (compare strychnia). Bicarbonate of soda fails to precipitate acid solutions of salts of brucia. But this alkaloid separates (after a considerable lapse of time, with the escape of carbonic acid) in regular, and comparatively large crystals.

6. *Concentrated nitric acid* dissolves brucia, and its salts to intensely red fluids, which subsequently acquire a yellowish red tint, and become completely yellow upon the application of heat. Upon addition of protochloride of tin, or hydrosulphuret of ammonia, to this yellow fluid, (no matter whether concentrated or diluted with water,) the faint yellow colour changes to a most intense violet.

7. *Concentrated sulphuric acid* dissolves brucia to a faint rose-colored fluid.

8. The addition of iodic acid to solutions of a salt of brucia

produces no visible alteration in the cold, but, upon boiling, the fluid acquires a wine-red tint.

9. *Sulphocyanide of potassium* produces in concentrated solution of salts of brucia immediately, and in dilute solutions, after some time, a granular crystalline precipitate, which, when viewed under the microscope, appears composed of variously aggregated polyhedral crystalline grains. Friction applied to the sides of the vessel promotes the separation of the precipitate.

10. *Perchloride of mercury* produces also a white granular precipitate, which, when viewed under the microscope, appears composed of small round-shaped crystalline grains.

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c. VERATRIA (formula not yet settled) Ve.

1. Veratria appears generally as a pure white, yellowish, or greenish white powder, of acrid and burning (but not bitter) taste and exceedingly poisonous action. Veratria acts with great energy upon the membranes of the nose ; even the most minute quantity of the powder excites the most violent sneezing. It is insoluble in water ;. dissolves readily in alcohol, but more sparingly in ether. At a temperature as low as 122° it fuses like wax and solidifies upon cooling, to a transparent yellow mass.

2. Veratria neutralizes acids completely. Some salts of veratria are crystallizable, others dry up into a gummy mass. They are soluble in water, and of acrid, and burning taste.

3. *Potassa, ammonia*, and the *simple carbonates of the alkalies* produce in solutions of salts of veratria, a flocculent white precipitate, which viewed under the microscope, immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its appearance, and small scattered clusters of short prismatic crystals are observed, instead of the original coagulated flakes. The precipitate does not redissolve in an excess of potassa, and carbonate of potassa. It is slightly soluble in ammonia, in the cold, but the dissolved portion separates again upon application of heat.

4. With *bicarbonate of soda*, and *bicarbonate of potassa*, vera-

tria comports itself like strychnia, and brucia. It separates how-
ever readily, upon ebullition, even from dilute solutions.

5. If veratria is acted upon with *concentrated nitric acid*, it
agglutinates at first into small resinous lumps, which afterwards
dissolve slowly in the acid. The solution presents a faint red-
dish yellow color.

6. When acted upon with *concentrated sulphuric acid*, veratria
agglutinates also into resinous lumps at first, which afterwards dis-
solve with great readiness to a pale yellow fluid, the color of which
gradually increases in depth and intensity, changing afterwards to
a reddish-yellow, then to an intense blood red, subsequently to
crimson, and becoming finally violet.

7. *Sulphocyanide of potassium* produces only in highly con-
centrated solutions of salts of veratria flocculent gelatinous pre-
cipitates.

Recapitulation and Remarks.

The alkaloids of the third group are also precipitated by many
other reagents besides those above mentioned, as, for instance, by
tincture of galls, bichloride of platinum, &c. But the universality
of these reactions render them of little importance in an analytical
point of view.

Strychnia may be separated from brucia, and veratria by means
of absolute alcohol, since it is insoluble in that menstruum whilst
the two latter alkaloids readily dissolve in it. The identity of
strychnia is best established by the reaction with sulphuric acid
and chromate of potassa; as also by the form of its crystals
viewed under the microscope, or finally by the form of the preci-
pitate which sulphocyanide of potassium, and perchloride of
mercury produce in solutions of its salts. Brucia, and veratria are
not readily separated from one another, but may be detected side
by side. The identity of brucia is best established by the reac-
tions with nitric acid and protochloride of tin, with hydro-sulphuret
of ammonia, or by the crystalline form of the precipitate which
ammonia produces in solution of salts of brucia. Veratria is
sufficiently distinguished from brucia, and the other alkaloids
which we have treated of, by its characteristic deportment at a

gentle heat, and also by the form of the precipitate which alkalies produce in solutions of its salts. To distinguish veratria by the side of brucia, the reaction with sulphuric acid is employed.

To these alkaloids, I will add *salicine*, although this substance does not properly belong to the same class of chemical compounds with the alkaloids.

§ 138.

SALICINE ($C_{26} H_{18} O_{14}$)

1. Salicine appears either in the form of white crystalline needles, and scales of silky lustre, or, in cases where these crystals are very small, as a powder of silky lustre—it has a bitter taste, is readily soluble in water, and alcohol, but insoluble in ether.

2. No reagent precipitates salicine as such.

3. Salicine, when acted upon with *concentrated sulphuric acid*, agglutinates into lumps like resin, and acquires an intensely blood red color, without dissolving in the acid; the color of which remains unaltered.

4. If an aqueous solution of salicine is mixed with *hydrochloric acid, or dilute sulphuric acid*, and the mixture boiled for a short time, the fluid suddenly becomes turbid, and deposits a fine granular crystalline precipitate (saliretine).

SYSTEMATIC COURSE LEADING TO THE DETECTION OF THE ALKALOIDS TREATED OF IN THE FOREGOING PARAGRAPHS, AND OF SALICINE.

§ 139.

The analytical course which I am now about to describe is based upon the supposition that the analyst has to examine a concentrated solution of one, or several salts of the alkaloids which solution is free from any admixture of substances which might tend to obscure, or modify the reactions. For the modifi-

cations which the presence of coloring or extractive matter, &c. requires, I refer to § 142.

I. DETECTION OF THE ALKALOIDS, AND OF SALICINE, IN SOLUTIONS SUPPOSED TO CONTAIN BUT ONE OF THESE SUBSTANCES.

§ 140.

1. Dilute solution of potassa is added drop by drop to a portion of the aqueous solution, until the fluid acquires a scarcely perceptible alkaline reaction.

    a. NO PRECIPITATE IS FORMED; this proves the total absence of the alkaloids, and indicates the presence of SALICINE. To set all doubt at rest on this point, the original solution is tested with concentrated sulphuric acid, and with hydrochloric acid, according to the directions of § 138, 3. and 4.

    b. A PRECIPITATE IS FORMED. Potassa is added drop by drop, until the fluid manifests a strongly alkaline reaction.

        a. The precipitate redissolves: MORPHIA. To arrive at a positive conclusion on this point, another portion of the solution is tested with iodic acid (§ 135. 8.), and a portion of the original substance with nitric acid, (§ 135. 6.)

        β. The precipitate remains undissolved: Presence of an alkaloid of the second or third group. Pass over to 2.

2. A second portion of the original solution is acidified with from two to three drops of dilute sulphuric acid, and a saturated solution of bicarbonate of soda then added until the acid reaction is exactly neutralized; the inner sides of the vessel are then strongly rubbed, and the mixture allowed to stand at rest for half an hour.

    a. NO PRECIPITATE IS FORMED : Absence of narcotina, quina, and cinchonia. Pass over to 3.

    b. A PRECIPITATE IS FORMED : Narcotina, quina, or cinchonia. A portion of the original solution is mixed with an excess of ammonia, a sufficient quantity of ether added, and the mixture shaken.

a. The precipitate which forms at first upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers. Narcotina or quina. The test-tube is placed in hot water to evaporate the ether, care being taken to maintain the ammonia in sufficient excess. If a precipitate separates, this is NARCOTINA. The reaction described at § 136. *a.* 5. may serve as a conclusive proof of the presence of this substance. If no precipitate separates, the analyst may conclude that QUINA is present. To set all doubt at rest on this point, the ammoniacal solution (which has been nearly evaporated to dryness) is very slightly acidified with one or two drops of acetic acid, and subsequently precipitated with carbonate of potassa; the precipitate is finally inspected under the microscope. (Compare § 136. *b.* 3.)

β. The precipitate which forms upon the addition of ammonia does not redissolve in the ether: CINCHONIA. The deportment of cinchonia when heated (the exhalation of a peculiar aromatic odor) may serve as a conclusive test, (§ 136. *c.* 3.)

3. A portion of the original substance, or of the residue which will remain upon evaporating the solution, is placed in a watch-glass, and treated with concentrated sulphuric acid.

a. A colorless solution is obtained, which, upon application of heat, changes to a faint olive green : STRYCHNIA. The reaction with sulphuric acid, and chromate of potassa is resorted to as a conclusive test, (§ 137. *a.* 8.)

b. A rose-colored solution is obtained, which becomes deep red upon addition of nitric acid : BRUCIA. The reaction with nitric acid, and protochloride of tin is resorted to as a conclusive test, (§ 137. *b.* 6.)

c. A yellow solution is obtained, the color of which changes to a yellowish red, then to blood red, and turns afterwards crimson : VERATRIA.

II. DETECTION OF THE ALKALOIDS, AND OF SALICINE IN SOLU-
TIONS, WHICH ARE SUPPOSED TO CONTAIN SEVERAL, OR THE WHOLE
OF THESE SUBSTANCES.

§ 141.

1. Dilute solution of potassa is dropped into a portion of the
aqueous solution, until the fluid acquires a scarcely perceptible
alkaline reaction.

    a. No PRECIPITATE IS FORMED : This proves the total
absence of the alkaloids, and indicates the presence of SALI-
CINE. The reactions with concentrated sulphuric acid, and
with hydrochloric acid are resorted to as conclusive tests.
(Compare § 138. 3. and 4.)

    b. A PRECIPITATE IS FORMED : Potassa is added drop by
drop until the fluid manifests a strongly alkaline reaction.

        a. The precipitate redissolves. Absence of the alkaloids
of the second and third group. Presence of MORPHIA.
The reactions with iodic acid (§ 135. 8.) and with nitric
acid (§ 135. 6.) are resorted to as conclusive tests. Exa-
mination for salicine, vide 4.

        *β. The precipitate does not redissolve, or at least not
completely.* The fluid is filtered from the precipitate, and
the latter treated as directed at 2. The filtrate is mixed
with bicarbonate of soda or bicarbonate of potassa, the
mixture heated to boiling, and maintained in ebullition
until evaporated nearly to dryness. The residue is treated
with water. If it dissolves completely, this is a sign that
no morphia is present; but if there is an insoluble residue,
this indicates the presence of morphia. The reactions with
iodic acid (§ 135. 8.) and with nitric acid (§ 135. 6.) are
resorted to as conclusive tests.

2. The precipitate of 1. *b. β.* is washed with cold water and
dissolved in a slight excess of dilute sulphuric acid ; solution of
bicarbonate of soda is added to the fluid until the acid reaction is
neutralized ; the mixture is stirred, the sides of the vessel being
vigorously rubbed, and the fluid then allowed to stand at rest for
half an hour.

a. No PRECIPITATE IS FORMED. Absence of narcotina, cinchonia, and quina. The solution is heated to boiling, and kept in ebullition until evaporated nearly to dryness. The residue is treated with cold water. If it dissolves completely, pass over to 4.; but should there be an insoluble residue, this is to be tested for strychnia, brucia, and veratria, according to the directions of 3.

b. A PRECIPITATE IS FORMED. The fluid is filtered from the precipitate, and the filtrate subsequently treated as directed at § 141. 2. *a.* The precipitate is washed with cold water, and then dissolved in a little hydrochloric acid; ammonia in excess is added to the solution, and subsequently a sufficient quantity of ether.

α. *The precipitate which forms at first upon the addition of the ammonia, redissolves completely in the ether, and the clear fluid presents two distinct layers.* Absence of cinchonia; presence of quina, or narcotina. The individual detection (and respective separation) of these two substances is then effected as directed at § 140. 2. *b.* α.

β. *The precipitate produced by the ammonia does not redissolve in the ether, or at least not completely :* CIN-CHONIA. Quina, or narcotina may also be present. The fluid is filtered from the undissolved precipitate, and the filtrate tested for quina, and narcotina, as at α. The precipitate consists of cinchonia. To set all doubt on this point at rest, the precipitate is cautiously heated, when the exhalation of a peculiar aromatic odor will demonstrate the presence of cinchonia. (Compare § 136. *c.* 3.)

3. The insoluble residue remaining upon evaporation of the solution of 2. *a.*, or of the filtrate of 2. *b.*, is dried in the water bath, and subsequently digested with absolute alcohol.

a. IT DISSOLVES COMPLETELY : Absence of strychnia; presence of brucia, or veratria. The alcoholic solution is evaporated to dryness, in the water bath, the residue divided into two portions, one of which is tested for BRUCIA, with nitric acid, and protochloride of tin, (§ 137. *b.* 6), and the other for VERATRIA, by means of concentrated sulphuric acid, (§ 137. *c.* 6.)

b. It does not dissolve, or at least not completely :
STRYCHNIA. Brucia, and veratria may likewise be present.
The fluid is filtered from the residue, and the filtrate subse-
quently examined for BRUCIA, and VERATRIA according to the
directions of § 141. 3. *a.* The identity of the precipitate with
strychnia is demonstrated by the reaction with sulphuric acid,
and chromate of potassa, (§ 137. *a.* 8.)

4. A portion of the original solution is mixed with hydrochloric
acid, the mixture heated to boiling, and kept some time in ebulli-
tion. The formation of a precipitate demonstrates the presence of
SALICINE. To set all doubt on this point at rest, the original sub-
stance is tested with concentrated sulphuric acid, (§ 138. 3.)

DETECTION OF THE ALKALOIDS IN PRESENCE OF COLORING,
AND EXTRACTIVE VEGETABLE, OR ANIMAL MATTERS.

§ 142.

The presence of mucilaginous, extractive, and coloring matters
renders the detection of the alkaloids a task of considerable diffi-
culty. These matters obscure the reactions so much that we are
even unable to determine by a preliminary experiment, whether
the substance under examination contains one of the alkaloids we
have treated of in the foregoing paragraphs, or not. The best
method of preparing substances containing these extraneous mat-
ters in admixture, for subsequent analysis in the usual way, is
that recommended by MERCK, which I will give here with a few
modifications.

The substance under examination is mixed with concentrated
acetic acid to strongly acid reaction, and the mixture digested
for several hours. The fluid is strained from the solid part, and
the latter washed with water acidified with acetic acid. The whole
of the fluid obtained is evaporated to dryness in the water bath.
The residue is boiled first with spirits of wine alone, and subse-
quently with spirits of wine containing an admixture of acetic acid ;

the whole of the solution thus obtained is evaporated nearly to
dryness in the water bath, again diluted with water, carbonate
of potassa added to feebly alkaline reaction, the mixture eva-
porated to a syrupy consistence, and allowed to stand at rest
for twenty-four hours; it is then again diluted with water, and
the fluid is filtered from the precipitate which has been formed
in the process ; the precipitate is washed with water, and di-
gested with concentrated acetic acid ; the solution obtained
is diluted with water, decolorized with pure animal charcoal,
and finally examined in the usual way for the alkaloids, and for
salicine.

II.

GENERAL PLAN OF THE ORDER, AND SUCCESSION IN WHICH
SUBSTANCES OUGHT TO BE ANALYSED FOR PRACTICE.

IT is not a matter of indifference whether the student, in ana-
lysing for the sake of practice, follow no rule, or order whatever
in the selection of the substances which he intends to analyze, or
whether, on the contrary, his investigations and experiments
proceed systematically. Many ways indeed may lead to the
desired end, but one of them will invariably prove the shortest.
I will therefore here point out a course which experience has
shown to lead safely, and speedily to the attainment of the object
in view.

Let the student take one hundred compounds, arranged in
systematic order, (vide infra,) and let him analyze these com-
pounds successively in the order in which they stand arranged.
A careful and diligent examination of these will be amply suffi-
cient to impart to him the necessary degree of skill in practical
analysis. When analysing for the sake of practice only, the

student must above all things possess the means of verifying the results obtained by his experiments. The compounds to be examined ought, therefore, to be mixed by a friend who knows their exact composition.

A. *From 1 to 20.*

AQUEOUS SOLUTIONS OF SIMPLE SALTS : e. g. sulphate of soda, nitrate of lime, chloride of copper, &c. These investigations will serve to teach the student the method of analysing substances soluble in water, containing but one base. In these investigations it is only intended to ascertain which base is present in the fluid under examination ; but neither the detection of the acid, nor the proof of the absence of all other bases besides the one detected, are required.

B. *From 21 to 50.*

SALTS, &c., CONTAINING ONE BASE AND ONE ACID (in a solid form, as powder) : e. g. carbonate of baryta, borate of soda, phosphate of lime, arsenious acid, chloride of sodium, acetate of copper, sulphate of baryta, chloride of lead, &c. These investigations will serve to teach the student the method of effecting the solution of substances, and of detecting *one* acid, and *one* metallic oxide, even though the substance under examination be insoluble in water. The detection of both the base, and acid is required, but it is not necessary to prove that no other constituents are present.

C. *From 51 to 70.*

AQUEOUS, OR ACID SOLUTIONS OF SEVERAL BASES. These investigations will serve to teach the student the method of separating, and distinguishing several metallic oxides from one another. The proof is required that no other bases are present besides those detected. No regard is paid to the acids.

I. From 51 to 60. These are intended to teach the student

the method of separating the metallic oxides into the principal groups. The solutions consequently contain, e. g. potassa, lime, and lead; copper, iron, and arsenic; baryta, antimony, bismuth, and potassa, &c.

II. 61 to 70. These are intended to teach the student the method of effecting the individual, and separate detection of several bases belonging to one and the same group, and present in the same solution. The solutions contain, accordingly, e. g. potassa, soda, and ammonia; zinc, manganese, and nickel; copper, mercury, and lead; antimony, tin, arsenic, &c.

D. *From* 71 *to* 80.

AQUEOUS SOLUTIONS CONTAINING SEVERAL ACIDS EITHER IN THE FREE STATE, OR IN COMBINATION WITH BASES, e. g. sulphuric acid, phosphoric acid, and boracic, acid;—carbonic acid, sulphuretted hydrogen, and hydrocyanic acid; tartaric acid, citric acid, and malic acid; chlorine, iodine, and bromine; nitric acid, hydrochloric acid, and oxalic acid. These investigations are intended to teach the student the method of detecting the several acids present in the same solution. The proof is required that no other acids are present besides those detected. The bases are disregarded.

E. *From* 81 *to* 100.

ALLOYS, MINERALS, AND MIXTURES OF EVERY DESCRIPTION;— the investigations will serve for further practice, and to prove that the student has attained a certain degree of practical skill in qualitative analysis. All the constituents of the substance under examination must be detected, and the nature of the substance ascertained.

III.

ARRANGEMENT OF THE RESULTS OF THE ANALYSES PERFORMED FOR PRACTICE.

The manner in which the results of analytical investigations ought to be noted, and arranged, as long as the student analyzes for practice, is not a matter of indifference. The following examples will serve to illustrate the method which I have found the most appropriate in this respect.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS.

Nos. 1 *to* 20.

Colorless fluid of neutral reaction.

Cl H *no precipitate,* consequently no Ag O Hg_2 O	H S *no precipitate,* no Pb O ,, Hg O ,, Cu O ,, Bi O ,, Cd O	NH_4 S, HS *no precipitate,* no Fe O ,, Mn O ,, Ni O ,, Co O ,, Zn O	NH_4O, CO_2 and NH_4 Cl *a white precipitate,* consequently either Ba O, Sr O, or Ca O,
	,, $As O_3$,, $As O_5$,, $Sb O_3$,, $Sn O_2$,, Sn O ,, $Au O_3$,, $Pt O_2$	,, $Al_2 O_3$,, $Cr_2 O_3$	no precipitate by solution of sulphate of lime, consequently LIME. Confirmation by means of $\overline{O}$
	,, $Fe_2 O_3$		

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS.

Nos. 21— 50.

White powder melting in the water of crystallization upon ap-
plication of heat, and remaining unaltered—soluble in water
—reaction neutral.

Cl H	HS	NH$_4$ S, HS	NH$_4$O, CO$_2$ NH$_4$, Cl	2 Na O, PO$_5$, and NH$_3$
no preci-pitate.	*no preci-pitate.*	*no precipi-tate.*	*no precipi-tate.*	*a white precipitate,* consequently MAGNESIA.

The detected base being Mg. O, and the analyzed substance
being soluble in water, Cl, I, Br, So$_3$, NO$_5$, Ā, &c., are the only
acids, or metalloids that can be present. The absence of the
organic acids and of nitric acid has been proved already by the
preliminary examination.

Ba Cl produces a white precipitate which Cl H fails to dissolve;
consequently SULPHURIC ACID.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, Nos. 51—100.

A white powder, acquiring a permanent yellow tint upon application of heat. Before the blow-pipe, a ductile metallic grain, and yellow incrustation with white border upon cooling. Insoluble in water, effervescing with hydrochloric acid, incompletely soluble in this acid, readily soluble in nitric acid.

Cl H	HS	NH₄, S, HS		NH₄, O, CO₂	A fixed residue upon evaporation.	Hydrate of lime has failed to evolve ammonia.
White precipitate insoluble in an excess of the precipitant, unaltered by ammonia: LEAD—confirmation by means of SO_3.	Black precipitate, insoluble in hydrosulphuret of ammonia, readily soluble in nitric acid. Examination for Cu, Bi, and Cd, results negative.	White precipitate; solution of this in hydrochloric acid remains clear upon addition of potassa in excess.		White precipitate; upon dissolving this in hydrochloric acid and adding solution of sulphate of lime to the fluid, after some time a white precipitate forms: STRONTIA. Precipitation with sulphate of potassa, filtrate tested for lime, with Ō results negative.		
		NH_4 Cl no precipitate.	HS white precipitate: ZINC.			

Of the acids, carbonic acid has already been found. Of the remaining acids, the following cannot be present.

Organic acids: the preliminary examination has already proved their absence.

Nitric acid and chloric acid, because the analyzed substance is insoluble in water.

SH, Cl H, IH, Br H, because the analyzed substance was readily soluble in nitric acid.

Chromic acid: the white color of the analyzed compound proves the absence of this acid.

PO_5, BO_3, Ō might be present.

Examination for these three acids yielded negative results.

IV.

TABLE

MORE FREQUENTLY OCCURRING FORMS AND
COMPOUNDS OF THE SUBSTANCES TREATED OF IN THE
PRESENT WORK,

ARRANGED

WITH ESPECIAL REGARD TO THE CLASS, TO WHICH THEY RESPECTIVELY BELONG
ACCORDING TO THEIR SOLUBILITY

IN WATER, IN HYDROCHLORIC ACID, OR IN NITRIC ACID.

PRELIMINARY REMARKS.

THE class to which the several compounds respectively belong according to the division specified at § 109, is expressed by figures. Thus 1 or I means a substance soluble in water; 2 or II a substance insoluble in water, but soluble in hydrochloric acid, or nitric acid; 3 or III a substance insoluble both in water, and acids. For those substances which stand as it were, on the limits between the various classes, the figures of the classes in question are jointly expressed: thus 1—2 signifies a substance difficultly soluble in water, but soluble in hydrochloric acid, or nitric acid; 1—3 a body difficultly soluble in water, and of which the solu-

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bility is not increased by the addition of the acids; and 2—3 a substance insoluble in water, and difficultly soluble in hydrochloric acid, and in nitric acid. Wherever the deportment of a substance with hydrochloric acid differs materially from that which it exhibits with nitric acid, this is stated in the notes.

The roman figures denote officinal, and more commonly occurring compounds.

The haloid salts, and sulphur compounds are placed in the corresponding column of the protoxide, or of the peroxide. Most of the salts given are neutral, the basic, acid, and double salts, if officinal, are mentioned in the notes; the small figures placed near the corresponding neutral or simple salts, refer to these. Cyanogen, chloric acid, citric acid, malic acid, benzoic acid, succinic acid, and formic acid, are of more common occurrence in combination with a few bases only, and have therefore been omitted from the table. The most frequently occurring compounds of these substances are : cyanide of potassium I, ferrocyanide of potassium I, ferricyanide of potassium I, sesqui-ferrocyanide of iron (Prussian blue) III, ferrocyanide of zinc and potassium II— III, chlorate of potassa I, the alkaline citrates I, the alkaline malates I, permalate of iron I, the alkaline benzoates I, the alkaline succinates I, and the alkaline formiates I.

A TABLE OF THE MORE COMMONLY OCCURRING

	KO	NaO	NH₄O	BaO	SrO	CaO	MgO	Al₂O₃	MnO	FeO	Fe₂O₃	CoO	NiO	ZnO
	I	I	I	I	1	I-II	II	II	II	II	II	II	II	II
S	I	I	I	I	I	I-II	2		II	1I	II	15	16	II
Cl	I	I	I₁₂	I	I	I	1	1	I	I	I₁₂	I	I	1
J	I	1	1	1	1	1	1		1	1	1			1
SO₃	I₁	I	I₁₃	III	III	I-III	I	I₁₋₁₃	I	I	I	1	I	I
NO₅	I	I	1	I	I	I	1	1	I	1	1	I	1	1
PO₅	1	I₁₀	1₁₀	2	2	II₁₄	2	2	2	2	II	2	2	2
CO₂	I₂	I₁₁	I	II	II	II	II		II	2		2		II
C₂O₃	I₃	1	I	2	2	II	2	2	2	1-2	.2	2	2	2
BO₃	I₄	I₄	1	2	2	2	2	2	2	2	2	2	2	2
A̅	I	I	I	I	1	1	1	1		1	I	1	1	1
T̅	1₄₋₉	I₇	I₆	2	2	II	1-2	1	1-2	1-2	I₈	1		2
AsO₅	I	1	1	2	2	2	2	2	2	2	2	2	2	3
AsO₃	I	1	1	2	1	2				2		2	2	
CrO₃	I	1	1	2	2	1	I	2	1		1	2	1	

NOTES.

1. SULPHATE of potassa and alumina I.
2. Bicarbonate of potassa I.
3. Binoxalate of potassa I.
4. Tartarized borax I.
5. Bitartrate of potassa I.
6. Tartrate of potassa and ammonia I.
7. Tartrate of potassa and soda I.
8. Tartrate of potassa and peroxide of iron I.
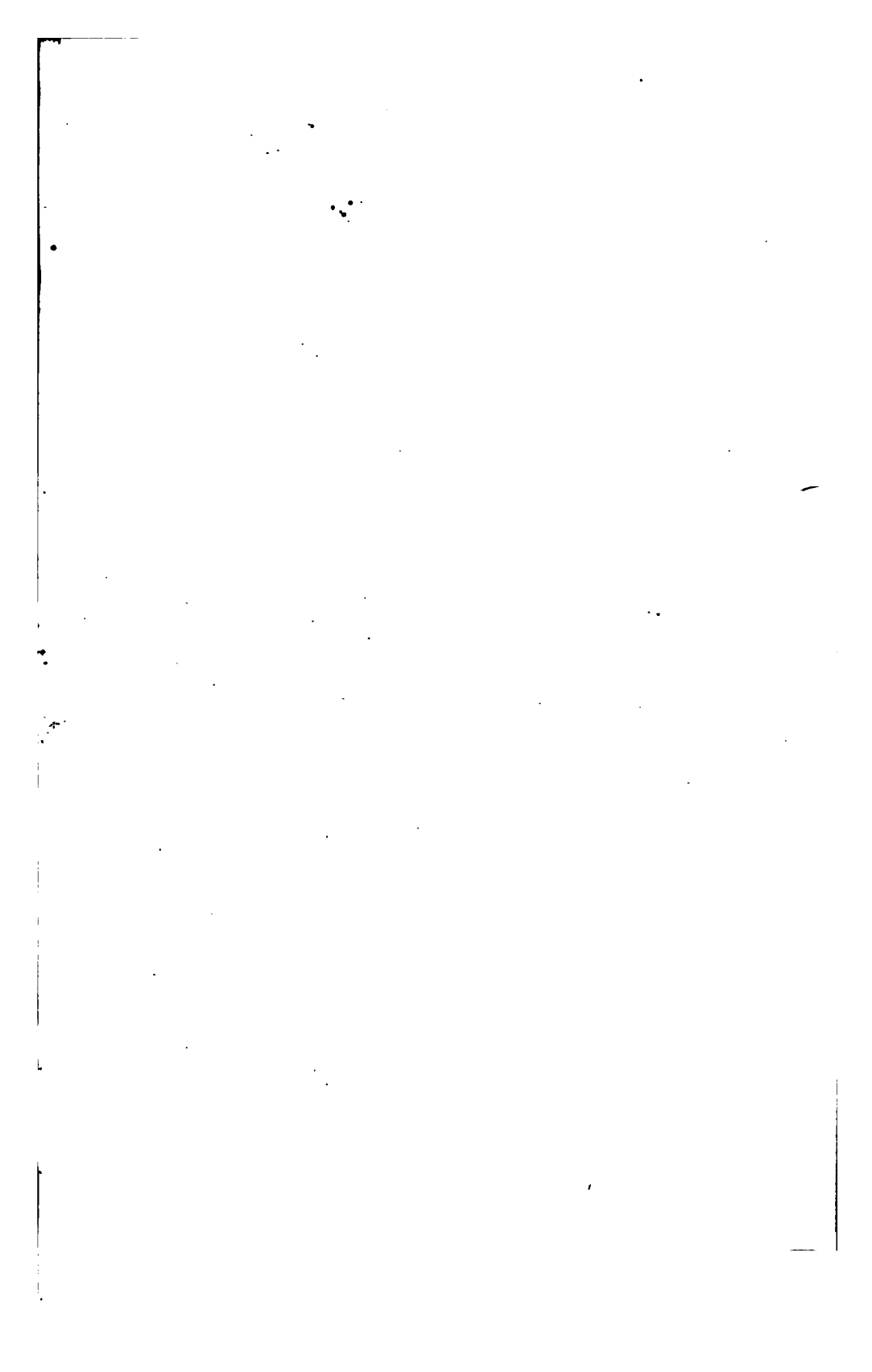9. Tartrate of antimony and potassa I.

FORMS AND COMBINATION OF BODIES.

	CdO	PbO	SnO	SnO$_2$	BiO$_3$	CuO	Hg$_2$O	HgO	AgO	PtO$_2$	AuO$_3$	SbO$_3$	Cr$_2$O$_3$
	2	II$_{18}$	2	2 & 3	2	II$_{22}$	II	II	2	2		$_{35}$	II&III
S	2	2	$_{20}$	$_{20}$	2	$_{23}$	III	III	$_{30}$	$_{31}$		II$_{36}$	
Cl	1	I-III	I	1	I	I$_{24}$	II-III	I$_{28}$	III	I$_{32\text{-}33}$	I$_{34}$	I$_{37}$	I
J	1	II	2	1			II		3				
SO$_3$	I	II-III	1		1	I$_{25}$	1-2	I$_{29}$	I-III	1		2	I
NO$_6$	1	I			I$_{21}$	I	I$_{27}$	I	1	1			I
PO$_6$	2	:2				2	2	2	2				2
CO$_2$	2	II			2	II	2	2	2				
C$_2$O$_3$	2	II	2		2	2	2	2	2			1-2	1
BO$_3$	1-2	2	2		2	2	1		2				2
$\overline{\text{A}}$	1	I$_{19}$	1	1	1	1$_{26}$	1-2	1	1			1	1
$\overline{\text{T}}$	1-2	2	1-2		2	1	1-2	2	2			I$_{38}$	1
AsO		2			2	2	2	2	2			2	1
AsO$_3$		2				II	2	2	2			2	
CrO$_3$		II-III	2		2	2	2	1-2	2			2	2

10. Phosphate of soda and ammonia I.
11. Bicarbonate of soda I.
12. Chloride of iron and ammonium I.
13. Sulphate of alumina and ammonia I.
14. Basic phosphate of lime II.
15. Sulphuret of cobalt is readily decomposed by nitric acid, but very difficultly by hydrochloric acid. This substance is not officinal.
16. The same applies to sulphuret of nickel.
17. Sulphuret of zinc. Readily soluble in nitric acid, somewhat difficultly soluble in hydrochloric acid.

18. Minium is converted by hydrochloric acid into chloride of lead, by nitric acid into oxide, which redissolves in an excess of the acid, and into brown peroxide of lead, which is insoluble in nitric acid.

19. Triacetate of lead I.

20. Sulphuret, and bisulphuret of tin are decomposed and dissolved by hydrochloric acid; by nitric acid they are converted into peroxide, which is insoluble in an excess of the acid. Sublimed bisulphuret of tin dissolves only in aqua regia.

21. Basic nitrate of bismuth II.

22. Ammoniacal oxide of copper 1.

23. Sulphuret of copper is difficultly decomposed by hydrochloric acid, but with facility by nitric acid.

24. Chloride of copper and ammonium 1.

25. Sulphate of copper and ammonia 1.

26. Basic acetate of copper, partially soluble in water, and completely in acids.

27. Basic nitrate of protoxide of mercury and ammonia II.

28. Basic chloride of mercury and ammonium II.

29. Basic sulphate of peroxide of mercury II.

30. Sulphuret of silver soluble only in nitric acid.

31. Sulphuret of platinum is not effected by hydrochloric acid; boiling nitric acid converts it into a soluble sulphate of peroxide of platinum.

32. Chloride of platinum and potassium 1—3.

33. Chloride of platinum and ammonium 1—3.

34. Chloride of gold and sodium I.

35. Oxide of antimony soluble in hydrochloric acid, but not in nitric acid.

36. Sulphuret of antimony and calcium 1—2.

37. Basic chloride of antimony II.

38. Tartrate of antimony and potassa I.